

# RECENT PROGRESS IN CHEMI-IONIZATION KINETICS†

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## ABSTRACT

A review of chemi-ionization reactions based on knowledge acquired since 1968 is given. Chemi-ionization reactions are considered to be: 'Reactions by which the number of elementary charge carriers is increased as the direct result of the formation of new chemical bonds'. This includes both associative ( $A + B \rightarrow AB^+ + e^-$ ) and rearrangement ( $A + BC \rightarrow AB^+ + C + e^-$ ) ionization reactions. Rate coefficients for these reactions are often on the order of  $10^{-12}$  to  $10^{-9}$  ml molecule $^{-1}$  sec $^{-1}$  and decrease with increasing temperature (relative collision velocity). For a given reactant A the rate coefficients also tend to decrease with an increasing number of atoms in B. A number of examples of exoergic chemi-ionization reactions between ground state reactants have now been definitely established. More detailed knowledge of reactions involving an electronically excited collision partner has become available and meaningful comparisons to Penning ionization can be made. However, our understanding of the details of the processes occurring are based primarily on observations of noble gas metastables, which, as is shown, do not in all respects apply to reactions of other species.

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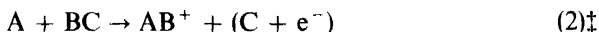
## I. INTRODUCTION

Chemi-ionization is a process by which the number of elementary charge carriers is increased as a direct result of the formation of new chemical bonds. Two elementary reaction types are covered by this definition:

*Associative ionization:*



*Re-arrangement ionization:*



A few years ago (1968–1969), this author summarized<sup>1</sup> knowledge of the hundred or so chemi-ionization reactions which had then been studied. It

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‡The parentheses in Reaction (2) indicate that the reaction may lead directly to the negative ion.

is the purpose of the present paper to discuss the developments in this area since then.

In environments where chemi-ionization is observed energy transfer ionization often can occur as well. This process is commonly referred to as Penning ionization.

*Penning ionization:*



The species B may be simply ionized in Reaction (3) or it may be ionized with subsequent dissociation to a smaller ion and neutral fragments<sup>2</sup>:

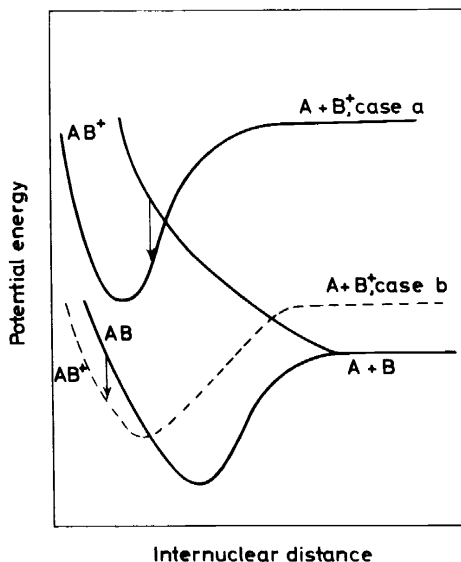
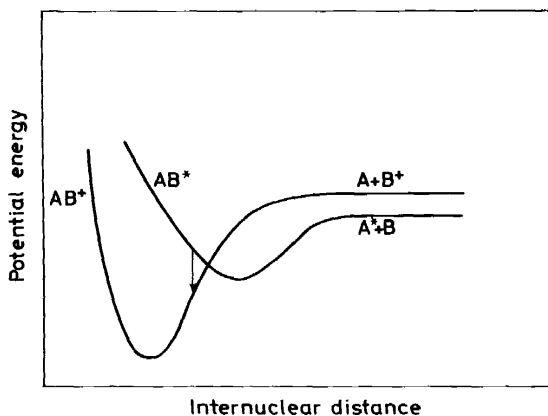


Figure 1. Schematic potential energy curves illustrating associative ionization paths for reactants in their ground internal energy states. The arrow indicates electron ejection. Case (a), solid line: endoergic reaction. Case (b), dashed line: exoergic reaction.

dissociation of B to a positive and a negative ion (ion-pair production) is another possibility (see, e.g., Ref. 3), as is  $A^+ + B^-$  formation (Ref. 1b). Penning ionization and other ionization processes are sometimes included in the term chemi-ionization<sup>4,5</sup>. While there is some theoretical justification for this, e.g. common entrance reaction channels are sometimes involved in Penning and 'true' chemi-ionization processes, it appears undesirable to broaden a term which has acquired a very specific meaning, as a result of a specific need among workers in the various fields of chemistry involving ionized gases. This paper is concerned with Penning ionization only to the extent that it bears on the discussion of reactions of types (1) and (2).

Several classes of chemi-ionization reactions can be distinguished on the basis of the electronic excitation energy, ( $E$ ), of reactant A and the ionization potential, ( $I.P.$ ), of reactant B. This may be shown on the basis of a few simplified potential energy curves for associative ionization. Electron ejection is in general a Franck-Condon process and is indicated as such by the arrows in the following figures. *Figure 1* illustrates the reactions (discussed in Section II) in which both reactants are in their ground state. With the  $AB^+$  curve positioned as in case (a) associative ionization is an endoergic process and requires a high relative velocity of the reactants. In case (b) the  $AB^+$  curve lies partly below the  $AB$  curve. In this region associative ionization is an exoergic process. When reactant A is electronically excited (Sections



*Figure 2.* Schematic potential energy curves illustrating associative ionization involving an excited reactant,  $E(A) < I.P.(B)$ . (After Herman and Cermak<sup>6</sup>).

III and IV), two situations can be recognized,  $E(A) < I.P.(B)$  (*Figure 2*) and  $E(A) \geq I.P.(B)$  (*Figure 3*). In the former case, exemplified by the formation of homonuclear diatomic ions [see, e.g., Reactions (31) and (32) below], Penning ionization cannot occur. In the latter case, Penning ionization competes with associative ionization. Two transitions are shown in *Figure 3*: In case (a) the energy of the ejected electron exceeds  $E(A) - I.P.(B) + E_K$  (the relative kinetic energy of  $A^*$  and B) and an associative ion  $AB^+$  is formed. In case (b) the energy of the electron is less than this quantity and a Penning ion  $B^+$  is formed, the additional energy becoming kinetic energy of the separating species A and  $B^+$ .

Since Ref. 1 was prepared, further review papers have appeared which cover selected areas of chemi-ionization in detail. Wexler<sup>9</sup> has reviewed ion (including chemi-ion) production in endoergic reactions of ground state reactants in molecular beams, where the necessary energy is provided by the relative kinetic energies of the reaction partners; interaction energies up to

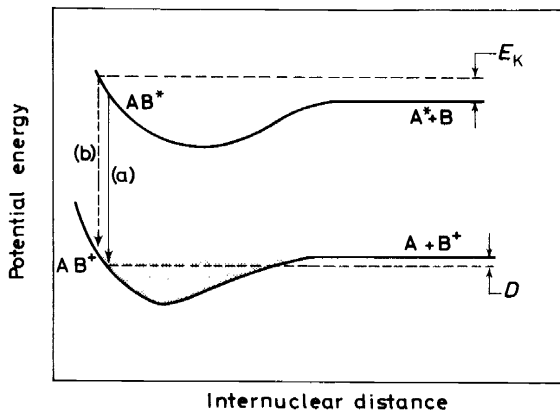


Figure 3. Schematic potential energy curves for the situation  $E(A) \geq I.P.(B)$ . Case (a), solid line: associative ionization. Case (b), dashed line: Penning ionization. (After Hotop and Niehaus<sup>7,8</sup>).  $D$  is the dissociation energy of  $AB^+$  formed in transition (a). For the sake of clarity,  $E_K$  is shown too large and is given for case (b) only.

about 20 eV, the upper limit for processes involving the formation of new chemical bonds, are covered. The production of ions in flames and the subsequent reactions of these ions have been discussed by Miller<sup>10</sup>, Calcote<sup>11</sup>, Calcote and Miller<sup>12</sup>, and Peeters, Vinckier and van Tiggelen<sup>13</sup>. Lampe's review<sup>2</sup> covers essentially the same period as Ref. 1 and is restricted to reactions of electronically excited species at near room temperature; it includes Penning reactions and emphasizes aspects other than those covered in Ref. 1, to which it thus represents a valuable complement. The article by Rundel and Stebbings<sup>5</sup> on collision processes involving metastable excited species includes a review of chemi-ionization and Penning ionization reactions of these species. The paper by Stedman and Setser<sup>14</sup> on the chemical reactions of the noble gas metastables provides a useful background for understanding the chemi-ionization reactions of these species.

The theoretical understanding of chemi-ionization has been summarized by Berry<sup>4</sup>. Since then, Miller *et al.*<sup>15-17</sup> have published a series of papers concerned with the theory of Penning ionization and associative ionization involving excited species. Hotop and Niehaus<sup>7,8</sup>, Micha, Tang and Muschlitz<sup>18</sup>, Olson<sup>19</sup>, and Cohen and Lane<sup>20</sup> have published in the same area. Myers and Young<sup>21</sup> have discussed the product energy distribution of endoergic atom-atom associative ionization reactions.

In much of the recent experimental work the state of the reactants has been known and the reaction products have been identified, sometimes including information on their excitation state. Such important details are mentioned below in the discussions of individual reactions. Most experiments have been performed in thermal systems in which the temperature was not specifically controlled but can be assumed to have been in the range of 300 to 500 K. Self-sustaining flame data were obtained predominantly at

temperatures in the 1800 to 3000 K range. Wherever other temperatures apply, specific mention is made of this fact.

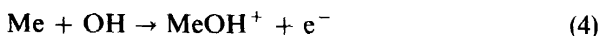
All rate coefficients are given below in ml-molecule-second units. Data from beam studies are usually quoted in the original articles as cross sections,  $Q(\text{cm}^2)$ . The  $Q$ -data resulting from thermal (i.e. not velocity-selected) beam work have, for the sake of uniformity, been converted in this paper to rate coefficients via the standard formula  $k = Q\bar{v} = Q(8kT/\pi\mu)^{\frac{1}{2}} = 1.46 \times 10^4 Q(T/\mu)^{\frac{1}{2}} \text{ ml molecule}^{-1} \text{ sec}^{-1}$ , where  $\bar{v}$  is the mean relative velocity of the reactants. However, for (the few) velocity selected beam studies only cross sections are meaningful and the data are reported in  $\text{cm}^2$ ; energies from such studies are reported in centre of mass units, corresponding to relative collision energies in bulk kinetics experiments.

In this review, the literature available up to May 1973 has been considered.

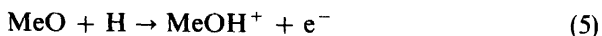
## II. REACTIONS WITH BOTH REACTANTS IN THE ELECTRONIC GROUND STATE

### A. Metallic species reactions

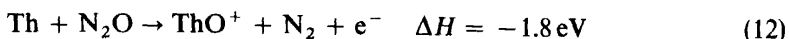
Since for most compounds the ionization potential exceeds the bond energies, the number of exoergic or near thermoneutral chemi-ionization reactions that can be anticipated between ground state neutral species is relatively small. Until recently no such reactions had been uniquely identified, though the formation of chemi-ions in hydrocarbon-oxygen reactions may be reasonably attributed to such a process (cf. Section II.B). Also, the presence of  $\text{MeOH}^+$  (Me denotes a metal atom) in alkaline earth seeded flames is due<sup>1c</sup> to either



or



where Reaction (4) is about thermoneutral for  $\text{Ba}^{22}$ . A deliberate search for exoergic neutral-neutral chemi-ionization reactions, based on known or anticipated favourable thermochemistry, is being made at several laboratories and has resulted in the discovery of:

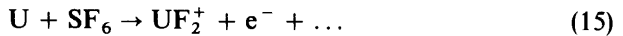


<sup>†</sup> Unless otherwise mentioned the  $\Delta H$  values quoted are from the original articles or the *JANAF* tables<sup>24</sup>.  $\Delta H$  values from other sources are quoted in ( ) after the  $\Delta H$  value.

Fite *et al.*<sup>27,28</sup> used crossed thermal beams with mass filter detection in the discovery of Reactions (6), (7), (8) and (9). They<sup>28</sup> determined  $k_6$  (1300 K) and  $k_7$  (600 K) to be  $2.0 \times 10^{-10}$  and  $1.0 \times 10^{-12}$  ml molecule<sup>-1</sup> sec<sup>-1</sup>, respectively. The latter is  $1.0 \times 10^{-2}$  times the rate coefficient for the total reaction between U and O<sub>2</sub>; the other reaction channel which leads to neutral products is



In a study of Reaction (7) using a chopped U beam and phase-sensitive detection it was shown<sup>28</sup> that all U atoms in the beam can participate in the UO<sub>2</sub><sup>+</sup> formation, not just those in the high-energy tail of the Boltzmann distribution: the activation energy is on the order of 0.01 eV or less. Following Fite and Irving's discovery of Reactions (6) and (7), Zavitsanos<sup>29</sup> established the occurrence of Reactions (10–12) in a bulk mixing chamber with mass spectrometric detection and determined that, at  $\approx 2300$  K,  $k_{11}/k_7 = 1.2 \pm 0.1$ . Further work by Fite and Kim<sup>30</sup> has shown the occurrence of:

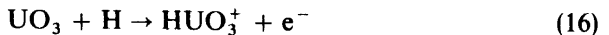


No ions could be detected<sup>30</sup> in U + N<sub>2</sub> or U + various hydrocarbon systems.

The above value of  $k_6$  is about equal to the collision frequency rate coefficient, while Reactions (7) and (11) occur about once in every 10<sup>2</sup> collisions. Such collision efficiencies are on the same order as those found for chemi-ionization reactions of excited species (cf. Ref. 1 and Sections III and IV below). Apparently then, fully-allowed exoergic chemi-ionization reactions are usually fast reactions. In excited atom reactions it may also be noted that chemi-ionization reactions involving molecular reactant partners often have lower rate coefficients than those with atomic partners (cf. Ref. 1a and Section III below).

The fact that the reverse processes of the above chemi-ionization reactions are endoergic implies that the chemi-ions (at least those formed in associative reactions) are stable against dissociative recombination at low energies. Combined with the fact that no excitation source is required to produce the ions this suggests that these reactions may be used for a practical plasma source (e.g. for the creation of ion clouds in the upper atmosphere at night)<sup>31</sup>. Materials requiring lower temperatures for their evaporation than U or Th would, however, be more practical if similar chemi-ionization reactions could be found for them.

Kelly and Padley<sup>32</sup> have found evidence for a homogeneous chemi-ionization process in the burnt gases of U salt-seeded fuel-rich, premixed atmospheric pressure hydrogen–oxygen–nitrogen flames. From the [H]-dependence of the ions they conclude that essentially the same mechanism is operative as previously observed upon alkaline earth addition to such flames [Reactions (4) and/or (5)]; specifically they suggest



or its UO<sub>2</sub> + OH equivalent. It seems unlikely that Reactions (6), (7) or (14) could play a major role in such burnt gases since [O], [O<sub>2</sub>], and [NO]

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are typically very low in these environments ( $< 10^{-3}$  [H] or [OH]) and the reactions of the species involved would not fit the observed kinetic behaviour. Jensen<sup>3,3</sup> has studied the addition of tetramethyltin [ $\text{Sn}(\text{CH}_3)_4$ ] to such hydrogen-oxygen-nitrogen flames and has mass spectrometrically identified  $\text{SnOH}^+$ , which is most likely due to the endoergic process

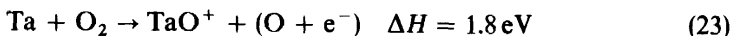
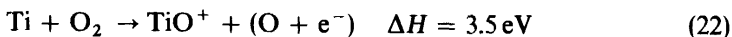
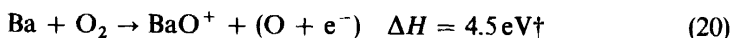


The Sn + OH route appears less likely since most of the tin is present as stannous oxide (SnO). Hayhurst and Kittelson<sup>34</sup> also conclude on the basis of a smaller steric factor that reactions of type (5) are generally more likely than those of type (4) in these burnt gas environments.

Knowledge of endoergic chemi-ionization reactions has further advanced in recent years with the appearance of beam techniques<sup>9</sup> for the 0.5 to 20 eV interaction energy range. Neynaber, Myers and Trujillo<sup>35</sup> have adapted the merging beams technique and observed via positive and negative ion mass spectrometry,



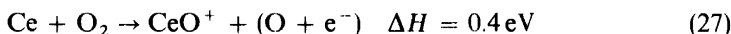
in addition to the  $\text{Na}^+ + \text{O}_2^-$ ,  $\text{Na}^+ + \text{O}_2 + \text{e}^-$  and  $\text{Na}^+ + \text{O} + \text{O}^-$  product combinations. The threshold energy for Reaction (18) is about 5.5 eV. The cross section reaches a maximum of  $4 \times 10^{-19} \text{ cm}^2$  at an interaction energy of 7 eV and the reaction is again undetectable above 8.5 eV. Cohen, Young and Wexler<sup>9,36,37</sup> used a crossed beam apparatus to determine mass spectrometrically the positive ions from the endoergic reactions of oxygen with barium, titanium, tantalum and aluminium. In addition to the dominant path, unipositive atomic ion production, the following reactions were also found to occur:



The threshold energies for Reactions (19), (20) and (21) were determined to be 0.2(-0.1, +1.0), 4.0 and 3(-1, +3) eV, respectively; these were determined from the angular distribution of the products for Reactions (19) and (21) and by using a velocity selected barium beam for Reaction (20). The total ion yields from tantalum were low, which may explain the absence of detectable quantities of  $\text{TaO}_2^+$ . Neither  $\text{AlO}^+$  nor  $\text{AlO}_2^+$  could be detected though yields in excess of  $2 \times 10^{-3}$  relative to  $\text{Al}^+$  would have been observable. The authors

<sup>†</sup>  $\Delta H$  values of reactions which may lead to negative ions are given in this manuscript on the basis of no negative ion formation. Since the electron affinity of O atoms is 1.4 eV,  $\Delta H$  of reactions leading to  $(\text{O} + \text{e}^-)$  has to be reduced by this amount for negative ion production reactions.

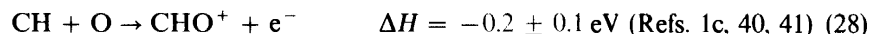
are continuing these studies for other Me-O<sub>2</sub> and Me-O and Me-OH systems and have recently shown<sup>9,37</sup> the occurrence of:



as well as confirmed Reactions (6) and (7).

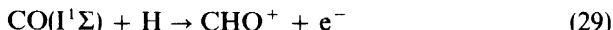
### B. Hydrocarbon, hydrogen and cyanogen combustion reactions

Chemi-ions are formed by hydrocarbon-oxygen combustion in self-sustaining flames<sup>10-13</sup>, shock waves<sup>38</sup> and detonation waves<sup>39</sup>, and in atomic oxygen-hydrocarbon reactions near 300 K<sup>1c</sup>. The major reaction responsible is commonly taken to be



Much circumstantial evidence, summarized in Ref. 1c, favours Reaction (28). Jonathan, Morris, Okuda and Smith<sup>42</sup> have recently measured the energy of the electrons produced in the atomic O-C<sub>2</sub>H<sub>2</sub>, C<sub>2</sub>H<sub>4</sub> and CH<sub>3</sub>C≡CH reactions. These chemi-electron spectroscopic experiments give further evidence for Reaction (28). The electron yield maximum was found to be 0.23 eV, with a half band width of 0.12 eV, for all three reactants. The coincidence of this energy with the exoergicity of Reaction (28) appears to rule out a substantial participation of excited CH, as had been suggested by Burke<sup>43</sup> to explain the observed splitting of atom cyclotron resonance signals from O-C<sub>2</sub>H<sub>2</sub><sup>44</sup>. It appears entirely possible that this conclusion of Jonathan *et al.* on the importance of ground state CH is applicable to high temperature hydrocarbon flames as well since chemiluminescence studies indicate that the same excited species are present in both systems.

Bayes<sup>45</sup> has suggested that since chemi-ionization accompanying hydrocarbon combustion involves (cf. Ref. 1c) one C, one H and one O atom the process



should also be considered. This suggestion is based on the observation of CO I<sup>1</sup>Σ (in at least the *v*' = 3, 6 states) in the O-C<sub>2</sub>H<sub>2</sub> reaction<sup>45</sup>. The subsequent measurements of Jonathan *et al.*<sup>42</sup> appear to argue against Reaction (29). The exoergicity of (29) would be 0.9, 1.3 and 1.6 eV, for I<sup>1</sup>Σ, *v*' = 0, 3 and 6, respectively, i.e. considerably higher than the chemi-electron spectra indicate. It appears highly unlikely that the reported Δ*H*<sub>f</sub>(CHO<sup>+</sup>) values could be sufficiently in error to allow for a substantial change in Δ*H* (29). Moreover since the I<sup>1</sup>Σ state is formed in a number of vibrational levels Reaction (29) would give rise to a broad band in the electron spectrum, not the observed single peak; this same argument would apply against major participation of other CO\* states formed in the O-C<sub>2</sub>H<sub>2</sub> reaction. Nonetheless, Bayes's suggestion underscores the need for a direct unambiguous demonstration of Reaction (28). Several investigators are planning such experiments<sup>46</sup>.



McGregor and Berry<sup>47</sup> have calculated  $k_{28}$  from a potential hyperface model for the ground state reactants. The rate coefficient curve deemed most probable gives values of about  $2.4 \times 10^{-12}$ ,  $7 \times 10^{-12}$ ,  $2.5 \times 10^{-11}$  and  $3.5 \times 10^{-11}$  ml molecule<sup>-1</sup> sec<sup>-1</sup> at 3, 25, 300 and 1000 K, respectively. No substantial rise in  $k$  appears to occur for  $T > 1000$  K. The 3 and 25 K values are of interest since Reaction (28) may be responsible for the formation of CHO<sup>+</sup> in interstellar space<sup>47,48</sup>. The values for  $T \geq 300$  K are in order of magnitude agreement with the estimates of  $5 \times 10^{-12}$  ml molecule<sup>-1</sup> sec<sup>-1</sup> (based on a calculation via microscopic reversibility on the isoelectronic reaction NO<sup>+</sup> + e<sup>-</sup> → N + O) by Bascombe, Green and Sugden<sup>49</sup> and  $3 \times 10^{-12}$  (from methane flame data) by Peeters, Vinckier and van Tiggelen<sup>13</sup>. Miller<sup>50</sup>, using best available [CH], [O] and ion production data from several laboratories has estimated  $k_{28} = 8 \times 10^{-13}$  ml molecule<sup>-1</sup> sec<sup>-1</sup>.

In hydrogen-oxygen flames without additives and impurities no chemi-ionization was thought to occur (see, e.g., Ref. 51). Hayhurst and Telford<sup>52</sup> have shown that the small amount of ionization they found to be residual in such flames may be attributable to



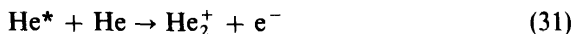
The product ion H<sub>3</sub>O<sup>+</sup> was identified mass spectrometrically and  $k_{30}$  was determined to be  $6.1 \times 10^{-36} \exp(-14000/T)$  ml<sup>2</sup> molecule<sup>-2</sup> sec<sup>-1</sup>. The low pre-exponential factor is indicative of a small reaction probability. Reaction (30) is in fact not a very likely elementary process; if it indeed represents an elementary reaction, it would be the only known example of a three-body chemi-ionization process (though others have been suggested)<sup>1</sup>.

As discussed in Ref. 1c chemi-ions are also produced in cyanogen flames. There have been further investigations of such flames<sup>53,54</sup> but it is not yet possible to suggest with a fair degree of confidence which elementary chemi-ionization reactions are involved.

### III. REACTIONS OF EXCITED ATOMS

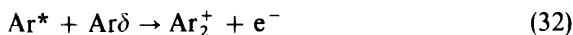
#### A. Noble gas atoms

In discussing the reactions of excited noble gas atoms it is useful<sup>1a</sup> to distinguish between the various types of excited states. These are (in sequence of increasing excitation energy): (i) the low-lying metastable states ( $2^3\text{S}$  and  $2^1\text{S}$  for He, and  $3^3\text{P}_2$  and  $3^3\text{P}_0$  for the other species)<sup>14</sup>, (ii) the short-lived higher excited states, (iii) the long-lived Rydberg states just below the ionization limit, and (iv) the auto-ionizing states. Formation of the homonuclear diatomic ions does not occur with the low-lying metastables<sup>1a</sup>; for example, the reaction



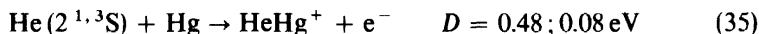
has been observed to occur only<sup>1a</sup> for the He ( $3^3\text{P}$ ) and higher excited  $n \geq 3$  states. Robertson *et al.* have now considerably improved their optical pumping experiments for measuring rate coefficients for the  $n = 3$  states in the positive column of a d.c. discharge in helium<sup>55</sup>. These states were selectively excited by modulated line absorption from the metastable  $2^1\text{S}$  and  $2^3\text{S}$  states.

By using phase-sensitive detection, the changes in excited-state populations were determined via emission spectroscopy while the in-phase variations in  $[\text{He}_2^+]$  were measured mass spectrometrically. The measured rate coefficients,  $k_{3,1}$ , for the  $3^3\text{P}$ ,  $3^1\text{P}$ ,  $3^3\text{D}$  and  $3^1\text{D}$  states are, respectively,  $3.2 \times 10^{-11}$ ,  $6.2 \times 10^{-11}$ ,  $9.0 \times 10^{-11}$  and  $4.0 \times 10^{-10}$  ml molecule $^{-1}$  sec $^{-1}$ . Collins, Johnson and Shaw<sup>56</sup> similarly used a frequency-doubled pulsed tunable dye laser to produce the ( $5^3\text{P}$ ) state and measured  $k_{3,1}$  for it. No direct product identification was made, but the result,  $k_{3,1} = 8 \times 10^{-11}$  ml molecule $^{-1}$  sec $^{-1}$ , is in reasonable agreement with the above  $n = 3$  measurements. An increase in  $k$  with increasing  $n$  is suggested by the work of Lampe's group<sup>57</sup>, utilizing single electron impact ionization chambers (in which both short and long-lived excited species can react). The results yield  $k_{3,1} = (2 \text{ to } 4) \times 10^{-9}$  ml molecule $^{-1}$  sec $^{-1}$ . This value for  $k_{3,1}$ , however, probably contains a considerable contribution from  $n > 5$  states. Lampe<sup>1a,58</sup> determined a  $k$  of  $(1 \text{ to } 2) \times 10^{-9}$  ml molecule $^{-1}$  sec $^{-1}$  for



Rate coefficients of this magnitude are on the order of hard sphere model gas kinetic collision frequencies for  $\text{He}^*$  and  $\text{Ar}^*$ , considering that the collision diameters of electronically excited atoms are much larger than those of ground-state atoms<sup>59</sup>.

In heteronuclear excited noble gas atom reactions the possibility for Penning ionization in addition to chemi-ionization exists when  $E(A) \geq I.P.(B)$ . As can be seen from *Figure 3* the energy of the electrons ejected is indicative of the process taking place. Electrons with energy in excess of  $E(A) - I.P.(B) + E_k$  correspond to chemi-ionization, i.e. to transitions into the bound (hatched) part of the  $A-B^+$  system. Electron spectroscopy thus can yield important information on the ionization process (as also discussed in Section II. cf. Ref. 42)—such spectroscopy is usually referred to as Penning electron spectroscopy by workers in the field of excited species collisions, a name originating from the pioneering work of Cermak<sup>60-62</sup>. Hotop and Niehaus<sup>7,8</sup> have further improved the technique and applied it to studies of the reactions of helium metastables. The dissociation energy of the chemions formed, ' $D$ ' in *Figure 3*, is found<sup>7</sup> to be on the order of thermal energies, i.e. less than 0.1 eV, for krypton and xenon as collision partners, indicating that the ions are formed either in electronic states having very shallow potential energy wells or in highly vibrationally and rotationally excited states. For a number of reactions with metal atoms somewhat higher  $D$ s have been found and absolute dissociation energies have been obtained<sup>8</sup>. The following values for  $D$  were measured [with the value given for  $\text{He}(2^1\text{S})$  preceding that of  $\text{He}(2^3\text{S})$ ]:

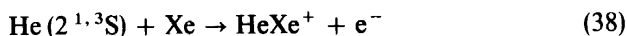
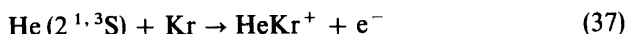
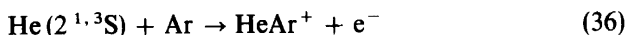


The accuracy of these data is given as  $\pm 0.05$  eV.

In accord with these small dissociation energies the fraction of ionizing

## RECENT PROGRESS IN CHEMI-IONIZATION KINETICS

collisions which produces associative ions decreases with increasing temperature (collision velocity). This was demonstrated by Hotop, Niehaus and Schmeltekopf<sup>63</sup> for the reactions:



The apparatus used was similar to that of Refs. 7 and 8, i.e. a thermal beam of helium metastables interacting in a collision chamber with the selected target species. A helium lamp between the excitation and reaction chambers allowed the removal of He(2<sup>1</sup>S) by optically pumping such atoms to a higher excited state, from which allowed transitions to the ground state

Table 1. Effect of temperature on the fraction of ionizing collisions of He(2<sup>1,3</sup>S) which proceed via chemi-ionization and on the relative rate coefficients for He(2<sup>3</sup>S) and (2<sup>1</sup>S)†§

Target gas	T <sub>He</sub>	$\frac{k_{2^1\text{S}(\text{C})}}{k_{2^1\text{S}(\Sigma)}}$	$\frac{k_{2^3\text{S}(\text{C})}}{k_{2^3\text{S}(\Sigma)}}$	$\frac{k_{2^3\text{S}(\text{C})}}{k_{2^1\text{S}(\text{C})}}$	$\frac{k_{2^3\text{S}(\text{P})}}{k_{2^1\text{S}(\text{P})}}$	$\frac{k_{2^3\text{S}(\Sigma)}}{k_{2^1\text{S}(\Sigma)}}$
Ar	320	0.17	0.13	0.66	0.91	0.87
	90	0.31	0.14	0.42	1.12	0.90
Kr	320	0.12	0.15	0.85	0.65	0.67
	90	0.31	0.19	0.30	0.58	0.49
Xe	320	0.022	0.10	2.9	0.58	0.63
	90	0.067	0.15	0.79	0.32	0.36

† Data from Hotop, Niehaus and Schmeltekopf<sup>63</sup>.

§ C denotes chemi-ionization; P, Penning ionization and Σ, total ionization.

occur<sup>63</sup>; the transit time between the two chambers is long compared to the radiative lifetime of species undergoing optically allowed transitions. For the work of Ref. 63 a mass spectrometer was also used and the helium ion beam could be cooled to 90 K (the average relative kinetic energy of the colliding particles is due mostly to helium ions because of the greater mass of the target atoms and their random motion). A comparison of the results obtained at 320 and 90 K is shown in Table 1. Columns 3 and 4 of this table clearly show the aforementioned increase in the relative chemi-ionization rate coefficients  $k(\text{C})/k(\Sigma)$  at the lower temperature; this effect is considerably more pronounced for 2<sup>1</sup>S than for 2<sup>3</sup>S atoms. Columns 5, 6 and 7 have been included to show the effect of the identity of the metastable on the chemi-ionization, Penning and total ionization rate coefficients. In general He(2<sup>1</sup>S) appears to be somewhat more reactive toward the other noble gases than (2<sup>3</sup>S), a result at variance with that of Muschlitz *et al.* given in Table I of Ref. 1 which was, contrary to their later work<sup>64</sup>, not corrected for destruction

of chemi-ions by background gas. It may also be seen from *Table 1* that the fraction of ionizing collisions which lead to chemi-ions decreases in general with the mass of the target atom in accord with the finding<sup>63</sup> that the corresponding electron distribution shifts towards lower energies.

Muschlitz *et al.*<sup>64</sup>, also using a mass spectrometer with separate excitation and collision chambers, have measured the ratio  $k(C)/k(\Sigma)$  at 330 K, using He(2<sup>1</sup>S), He(2<sup>3</sup>S) mixtures in the ratio 2:1. For Reactions (36) and (37) they obtained values in excellent agreement with (ten per cent less than) those of Ref. 63, interpolated to correspond to this mixture ratio. For Ne(<sup>3</sup>P<sub>2,0</sub>)-Ar and Kr they obtained for  $k(C)/k(\Sigma)$  0.34 and 0.32, respectively, i.e. at 330 K the relative probabilities for associative ionization are more than twice as high for neon as for the helium metastables.

Kramer, Herce and Muschlitz<sup>64</sup> additionally measured the rate coefficients for destruction of the associative ions formed by the target gases argon or krypton present in the collision chamber, e.g.  $\text{HeAr}^+ + \text{Ar} \rightarrow \text{He} + \text{Ar}^+ + \text{Ar}$ , as being on the order of  $10^{-8}$  ml molecule<sup>-1</sup> sec<sup>-1</sup>. These large values are in keeping with the above electron spectroscopic measurements which show that the associative ions are formed close to the dissociation limit, hence collisions transferring only small amounts of energy are sufficient to dissociate the ions. These authors<sup>64</sup> also cite the earlier work of Munson, Field and Franklin<sup>65</sup> who observed, in reactions of the helium and argon metastables, collisional breakup of  $\text{HeAr}^+$  on Ar but not of  $\text{HeNe}^+$  on Ne or  $\text{ArKr}^+$  on Kr. Since the metastable states of helium and argon are insufficiently energetic to Penning-ionize neon and krypton respectively, it appears that for conditions under which  $E(A) < I.P.(B)$  (i.e. for the conditions of *Figure 2*), more stably bound ions can be formed.

While a temperature increase thus favours Penning ionization the total ionization rate coefficient is also affected by temperature. This was demonstrated by Tang, Marcus and Muschlitz<sup>66</sup>, who added a velocity selector to the metastables beam section of their apparatus and studied the relative velocity dependence of the cross sections of the Ne(<sup>3</sup>P<sub>2,0</sub>) reactions in the thermal beam energy range ( $3 \times 10^4$  to  $2 \times 10^5$  cm sec<sup>-1</sup>, corresponding to  $10^{-2}$  to  $10^{-1}$  eV). The cross section was found to vary as  $\bar{v}^{-x}$  below  $\bar{v} = 6.5 \times 10^4$  cm sec<sup>-1</sup> and to rise slowly at higher relative velocities. The values of  $x$  obtained were 0.622, 0.728 and 0.874, respectively, for argon, krypton and xenon as the target gas. Theoretical models to describe this behaviour have been developed<sup>18,19</sup>. (The semi-empirical model of Micha *et al.*<sup>18</sup> also may be used to predict the branching ratios of Penning and associative ionization.) Cher and Hollingsworth<sup>67</sup>, using a flowing afterglow system, showed that for the reactions of He(2<sup>3</sup>S) with nitrogen, oxygen, carbon monoxide and carbon dioxide, leading to electronically excited Penning ions,  $k(P)$  is proportional to  $T^{1 \pm 0.5}$  from 300 to 530 K.

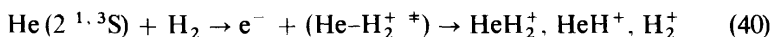
Howard, Riola, Rundel and Stebbings<sup>68</sup> using a crossed thermal beam apparatus with mass spectrometer detection have studied



at a mean interaction energy of 0.37 eV. They determined  $k(C)/k(\Sigma)$  values of  $0.10 \pm 15$  per cent and  $0.14 \pm 15$  per cent for He(2<sup>1</sup>S) and (2<sup>3</sup>S), respectively. Their measurements for  $k(\Sigma)$  for these two metastables are  $3 \times 10^{-9}$  and

$2 \times 10^{-9}$  ml molecule $^{-1}$  sec $^{-1}$ , respectively. These values are in good agreement with those calculated by Cohen and Lane<sup>20</sup>.

For polyatomic target species, re-arrangement type chemi-ionization reactions can occur in competition with associative and Penning ionization reactions. An example is the mass spectrometric study by Hotop and Niehaus<sup>69</sup> (discussed in Ref. 1a) on the He<sup>\*</sup>-H<sub>2</sub>(HD) system in which it was shown that all three types of ions are formed via a two-step process which may be summarized as:



where  $\ddagger$  indicates vibrationally excited H<sub>2</sub><sup>+</sup>. For collisions with H<sub>2</sub><sup>+</sup> in a sufficiently high vibrational excitation state HeH<sup>+</sup> will be the main chemi-ionization product; when hydrogen has essentially no vibrational energy HeH<sub>2</sub><sup>+</sup> can be formed<sup>4</sup>. From experiments with HD they also showed a strong hydrogen isotope effect on the ratio  $k(\text{C})/k(\text{P})$ , cf. Table V of Ref. 1. Using the apparatus of Ref. 63, Hotop and Niehaus<sup>70</sup> have now analysed the electron energy spectra arising from this reaction and have compared it to that obtained from photo-ionization of hydrogen. The energy shift in the He(2<sup>3</sup>S)-H<sub>2</sub> reaction is very small ( $0.09 \pm 0.01$  eV) and is common to all vibrational states<sup>†</sup>, from which it follows that, at the moment of electron ejection, the H<sub>2</sub> molecule is not considerably perturbed and that the bond formation between He and one or both H atoms occurs after the electron ejection. This picture has been confirmed in a merging beam study by Neynaber, Magnuson and Layton<sup>74</sup>, who compared the laboratory energy distributions of HeH<sup>+</sup> formed via Reaction (40) to that from



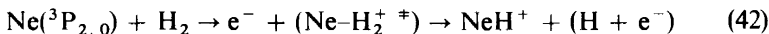
at interaction energies from 0.05 to 10 eV. Even though the distribution among vibrational states of H<sub>2</sub><sup>+</sup> is not identical in both cases, the energy distributions at 0.05 eV were very similar and those up to 2.0 eV were comparable. The energy distributions from the two reactions at 5 and 10 eV are quite different from each other, which suggests for Reaction (40) that some bonding of He and H<sub>2</sub> occurs before the electron is ejected. Neynaber *et al.* obtained a cross section of  $7 \times 10^{-17}$  cm<sup>2</sup> for HeH<sup>+</sup> formation via Reaction (40) at 1 eV. With thermal beams a value of  $3 \times 10^{-17}$  cm<sup>2</sup> has been obtained<sup>68</sup>. These data agree to within their combined uncertainty. Howard, Riola, Rundel and Stebbings<sup>68</sup> determined  $k_{40}(\text{He } 2\ ^3\text{S})/k_{40}(\text{He } 2\ ^1\text{S})$  to be near unity for HeH<sup>+</sup> production<sup>‡</sup>.

<sup>†</sup> The similarity in the vibrational distribution of the Penning and photo-electron spectra is in accord with the assumption that the ionization process is a Franck-Condon transition. Recently some exceptions to this usually valid rule have been demonstrated<sup>71-73</sup>. These were observed in the vibrational distribution of the electronically excited ions produced in the Penning reactions of He(2<sup>3</sup>S) with O<sub>2</sub>, Cl<sub>2</sub>, HCl and HBr and may be due to an added attractive component to the entrance channel caused by the interaction of the loosely bound outer electron of the excited He atom<sup>14</sup> with these electrophilic compounds.

<sup>‡</sup> These investigators<sup>68</sup> also determined this ratio for H<sub>2</sub><sup>+</sup> production and obtained a value of 1.2, about twice as high as that obtained with the flowing afterglow technique<sup>75</sup>. Similar differences between thermal beam and flowing afterglow Penning-ionization rate coefficient ratios for the helium metastables have been noted before and cannot yet be explained satisfactorily<sup>73</sup>. There are thus far no direct measurements of chemi-ionization rate coefficients via the flowing afterglow technique to determine whether similar discrepancies occur there.

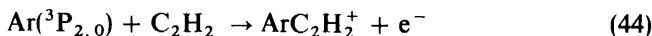
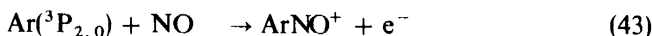
Information on the formation of  $H_2^+^*$  in Reaction (40) is available from the thermal  $He(2^{1,3}S)$  beam collision chamber work of Penton and Muschlitz<sup>76</sup>, who studied the isotope effect (relative rate coefficients for production of  $H_2^+$ ,  $HD^+$  and  $D_2^+$ ) in the  $He(2^{1,3}S)-H_2$ ,  $HD$  and  $D_2$  Penning reactions. These coefficients are in agreement with a model in which  $H_2^*$  is formed in a pre-ionizing Rydberg state with a lifetime longer than the collision time ( $10^{-12}$  to  $10^{-13}$  sec). This state can either form  $H_2^+ + e^-$  or dissociate to  $H + H^*$ . The ionization does not involve relative nuclear motion and hence is in first approximation independent of isotopic composition. However, dissociation does involve nuclear motion and hence its rate coefficient depends on isotopic composition. The ratio of rate coefficients of the dissociation process can be shown, on theoretical grounds, to be proportional to the square root of the ratio of the reduced masses of the collision partners<sup>7, 15</sup>; this prediction is in agreement with the experiments of Penton and Muschlitz<sup>76</sup>.

Rebick and Dubrin<sup>77</sup> using a fast beam-collision chamber apparatus studied  $NeH^+$  formation in the neon equivalent of (40),



with  $H_2$ ,  $HD$  and  $D_2$  in the relative kinetic energy range 2.5 to 17.1 eV. Hotop and Niehaus<sup>1a, 69</sup> had previously shown that at thermal energies this reaction proceeds via the same mechanism as (40). The cross section ratio  $Q(NeD^+)/Q(NeH^+)$  decreases with increasing collision energy which is in keeping with the spectator-stripping model in which the probability for a stabilized reaction product increases with decreasing reduced mass, i.e. with decreasing relative kinetic energy. The collision energy in these experiments exceeds the dissociation energy of ground state  $NeH^+$ ; it is likely that a substantial amount of the collision energy is carried away as kinetic energy of the electron (cf. also Ref. 74).

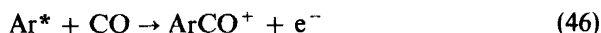
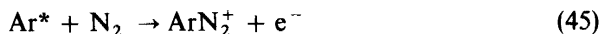
Holcombe and Lampe<sup>78</sup> have restudied:



using their pulsed single chamber mass spectrometer. Combining their estimated total ionization rate coefficients with  $k(C)/k(P)$  values obtained by Herman and Cermak<sup>1a, 79</sup> (0.2 and 0.6, respectively) yields  $k_{43} = 1 \times 10^{-11}$  ml molecule<sup>-1</sup> sec<sup>-1</sup> and  $k_{44} = 5 \times 10^{-12}$  ml molecule<sup>-1</sup> sec<sup>-1</sup>, in good agreement with Herman and Cermak<sup>79</sup>. This low  $k(C)/k(P)$  for chemi-ionization in  $Ar(^3P_{2,0})-C_2H_2$  collisions has been quantitatively confirmed in single-source mass spectrometer experiments by Jones and Harrison<sup>80</sup> and is in keeping with the observation<sup>1, 79</sup> that with an increasing number of atoms in the target molecule  $k(C)/k(P)$  decreases. However, it is useful to keep in mind that neutral dissociation reactions, which may be accompanied by excitation of products, often provide competitive pathways, even if  $E(A) > I.P.(B)$ . This has been pointed out by Stedman and Setser in their review of the reactions of metastable rare gas atoms<sup>14</sup>. Bolden *et al.*<sup>81</sup> have compared their flowing afterglow Penning ionization rate coefficients to rigid sphere collision rate coefficients for  $He(2^3S)$  with a number of molecules

and have found the ionization probability per collision to vary in the range 0.1 to 1.0. The flowing afterglow measurements of Schmeltekopf and Fehsenfeld<sup>75</sup> for He( $2^1, 3S$ ) are in the same range.

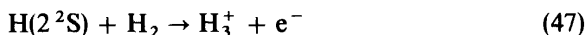
While it would appear that Penning ionization is generally favoured over associative ionization (at least above about 90 K), it should be kept in mind that such a generalization is based primarily on the reactions of rare gas metastables. Holcombe and Lampe<sup>58</sup> have studied the reactions:



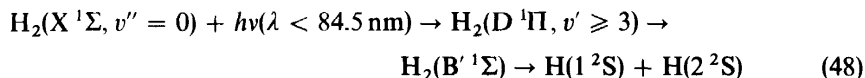
Ar( $3P_{2,0}$ ) has insufficient energy to Penning-ionize either nitrogen molecules or carbon monoxide. However, the higher excited states of argon have sufficient energy to Penning-ionize carbon monoxide and the highest excited states just below the ionization limit also could produce  $\text{N}_2^+$ . In their single chamber mass spectrometer study of reactions following impact of 30 eV electrons, these workers determined  $k_{45}$  and  $k_{46}$  to be equal, within experimental error, to  $k_{32} = 1.5 \times 10^{-9}$  ml molecule<sup>-1</sup> sec<sup>-1</sup>. The lifetime of the Ar\* states involved is on the order of  $10^{-6}$  sec, i.e. the observed processes (45) and (46) are dominated by the short-lived higher excited states. The near equality of these rate coefficients to each other and the near unit collision efficiency indicated by their magnitude suggest that associative ionization is more likely than Penning ionization for the non-metastable states of argon, at least for Ar\*-CO where Penning ionization could compete on the basis of the reaction energetics. The same conclusion can be drawn from the work of Hotop and Niehaus<sup>69</sup> (cf. Table V of Ref. 1) which shows that for the long-lived highly excited states of argon and krypton re-arrangement ionization dominates in the reactions with hydrogen, HD and D<sub>2</sub>, while for the helium and neon metastables Penning ionization dominates.

### B. Excited H and metal atoms

The decrease in chemi-ionization cross section with increase in relative velocity of the reactants has also been demonstrated by Chupka, Russell and Refaye<sup>1b, 82</sup> for the reaction of metastable H( $2^2S$ ) atoms with hydrogen



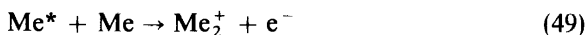
Translationally hot H( $2^2S$ ) atoms were produced via photodissociation



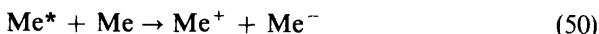
and the ions formed were detected mass spectrometrically. Comes and Wenning<sup>83</sup> have repeated this work using more accurate measurement methods and input data to obtain the population in  $D^1\Pi, v' = 3, 4$  and  $5$ . Their results are in only qualitative agreement with the earlier work. The ionization cross section is found to decrease as  $\bar{v}^{-x}$  ( $2 \leq x \leq 3$ ). For ( $D^1\Pi, v' = 3$ ) a cross section of  $10^{-17}$  cm<sup>2</sup> is found which combined with the calculated  $\bar{v} = 3.5 \times 10^5$  cm sec<sup>-1</sup> corresponds to  $k = 3.5 \times 10^{-12}$  ml molecule<sup>-1</sup> sec<sup>-1</sup>; the cross section for ( $D^1\Pi, v' = 5$ ) is smaller by a factor of ten.

The cross section for dissociative quenching of  $H(2^2S)$  by hydrogen leading to neutral H atoms is  $5 \times 10^{-15} \text{ cm}^2$  independent<sup>83</sup> of  $\bar{v}$ , hence the ionization step is a minor reaction path. Since  $E(H2^2S) < I.P.(H_2)$ , the reaction may be expected to proceed according to the path illustrated by *Figure 2*.

As discussed in Ref. 1b alkali metal vapours can be ionized by light of wavelengths longer than those corresponding to the atomic ionization potential. Specifically, such ionization has been observed for wavelengths corresponding to the principal series lines.  $n^2S_{\frac{1}{2}} \rightarrow m^2P_{\frac{1}{2}, \frac{3}{2}}$ . Appreciable ionization occurs only for the  $m \geq n + 2$  levels. The process responsible is

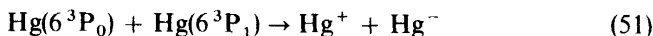


At wavelengths closer to the ionization limit atomic ion-pair formation



also occurs. Linevsky<sup>84</sup> has recently shown that at 1250 K, barium can be ionized by irradiation of barium lines connecting to the atomic ground state. The apparent onset for exoergic ionization occurs at 278.5 nm ( $6^1S - 8^1P$ ). No product identification was performed; if it is assumed that Reaction (49) is responsible, then the lower limit for the bond energy of  $Ba_2^+$  is 0.76 eV, very close to the values measured for the molecular alkali ions (0.79, 0.75, 0.73 and 0.70 eV for  $Na_2^+$ ,  $K_2^+$ ,  $Rb_2^+$  and  $Cs_2^+$ , respectively)<sup>1b</sup>. However, since barium oxides may have been present in the experiments other  $Ba^*$  reactions cannot be excluded<sup>84</sup>.

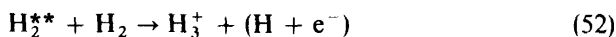
The conflicting evidence regarding the ionizing reaction between  $Hg(6^3P_0)$  and ( $6^3P_1$ ) atoms has been discussed in Ref. 1b. Klosterboer<sup>85</sup> has recently re-investigated this process and has come to the conclusion that the reaction responsible is ion-pair formation



rather than chemi-ionization. Thus there still is no established example of a chemi-ionization reaction involving two excited reaction partners.

#### IV. REACTIONS OF ELECTRONICALLY EXCITED MOLECULES

Hotop, Lampe and Niehaus<sup>86</sup> have studied reactions of long-lived excited  $H_2$  ( $HD$ ,  $D_2$ ) in an electron impact mass spectrometer with separate excitation and collision chambers. They found both reactions of metastable  $H_2^*$  with  $11.75 \leq E \leq 12.2 \text{ eV}$  (which they suggest is  $C^3\Pi$ ,  $v' = 0$  and in addition some other state) and long-lived highly excited  $H_2^{**}$  (probably at least in part above the first ionization limit<sup>87</sup>). For the latter they confirmed the occurrence of



previously observed by Chupka, Russell and Refaye<sup>1b, 82</sup>. No other chemi-ionization reaction due to  $H_2^{**}$  is reported in Ref. 86 beyond the observation that the ion production rate from such molecules is, in their apparatus, about two orders of magnitude lower than that from  $H_2^+$ . The results for a large

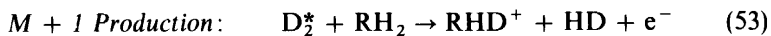


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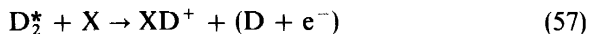
Table 2. Relative abundances of ions produced in reactions of long-lived excited  $D_2^*$  molecules. The abundance of the Penning ion with mass  $M$  is taken as unity.  $E(D_2^*)$  is larger than the  $I.P.$  of the molecules above the dashed line and smaller than the  $I.P.$  of the molecules below the line. For the latter, molecule-ions of mass  $M$  were produced by  $D_2^{*+}$ . (Data from Hotop, Lampe and Niehaus<sup>86</sup>).

Target molecule, $M$	Ion mass			
	$M + 1$	$M + 2$	$M + 3$	$M + 4$
$C_2H_2$	0.095	0.25	0.04	<0.001
$CH_3C \equiv CH$	0.04	0.17	0.01	—
$NH_3$	<0.01	0.14	<0.001	—
$C_2H_4$	$\approx 0.01$	0.062	—	—
$C_3H_6-1$	$\approx 0.02$	0.055	—	—
$C_4H_8-1$	$\approx 0.01$	0.03	—	—
$C_6H_{12}-1$	<0.01	<0.01	—	—
$O_2$	—	0.1	—	—
$H_2O$	—	1.89	—	—
$HCl$	0.10	0.46	—	—
$CO_2$	—	0.44	—	—
$CO$	—	1.17	—	—

number of  $D_2^*$  reactions are summarized in Table 2. From the fact that chemions are produced even for molecules as large as butene-1 it may be concluded that the probability for production of such ions upon collision with  $D_2^*$  is larger than for the analogous process involving excited noble gas atoms. As in the latter case, the probability of ionization decreases with the number of atoms in the target molecule. The fraction of ionizing collisions which leads to Penning ions is still considerably higher than that which yields chemions, at least for the target molecules above the dashed line, i.e. for the molecules of the general formula  $RH_2$  which have an  $I.P. < E(D_2^*)$ . The occurrence of the following reactions can be derived from the fact that for these molecules ions of masses  $M + 1$ ,  $M + 2$  and  $M + 3$  are produced:



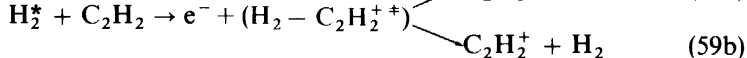
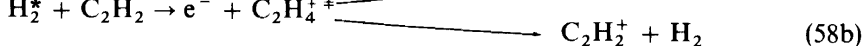
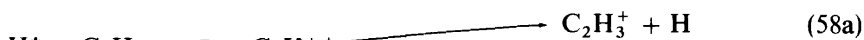
These reactions and Penning ionization (production of ions with mass  $M$ ) are energetically possible for all these  $RH_2$  molecules. For the group of reactions below the dashed line in Table 2 Penning ionization is not possible with  $D_2^*$ . The observation of  $M + 2$  ions therefore is indicative of the process



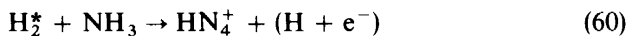
which indicates that the proton affinity ( $P.A.$ ) of  $X$  is larger than  $I.P.(D) + D(D_2) - E(D_2^*) = 6.2 \pm 0.2 \text{ eV}$ . For water molecules this affinity is known to

be 7.3 eV; for the other molecules a lower limit for the *P.A.* is thus obtained.

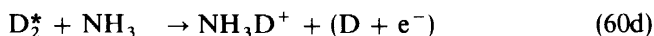
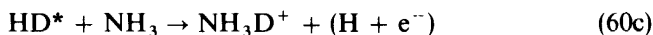
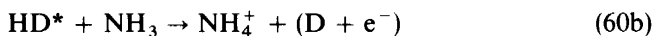
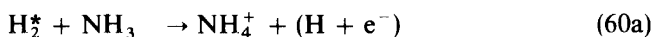
The reactions of acetylene and ammonia have been studied in greater detail by measuring the relative abundances of the ions produced by collisions with  $H_2^*$ ,  $HD^*$  and  $D_2^{*86}$ . The following reactions are proposed for acetylene:



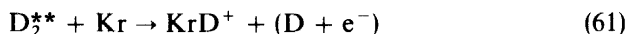
and their  $HD^*$  and  $D_2^*$  equivalents. Reaction (58) involves formation of a complex which dissociates within  $10^{-6}$  sec. Reaction (59) is similar to (40), i.e. the ionization of the target molecule precedes further reaction. As in the case of Reaction (40),  $k(C)/k(P)$  from (59) is strongly subject to the isotopic composition of the hydrogen molecule;  $k(C)/k(P)$  from (58) has only a weak isotope dependence.  $NH_4^+$  is probably formed directly in a stripping reaction,



A number of further  $D_2^*$  reactions were observed in Hotop's thesis work<sup>88</sup> and are given in Table 6 of Lampe's review<sup>2</sup>, which also lists (from data of Refs. 86, 88) the rate coefficients obtained for the various modifications of Reaction (60):



These are  $1.3 \times 10^{-10}$ ,  $0.54 \times 10^{-10}$ ,  $0.47 \times 10^{-10}$  and  $0.71 \times 10^{-10}$  ml molecule<sup>-1</sup> sec<sup>-1</sup>, respectively. Finally, Lauterbach<sup>87</sup> using a single excitation-collision chamber mass spectrometer has found strong evidence for



## V. CONCLUSION

The large amount of new data discussed in this paper testifies to the rapid developments in the field of chemi-ionization kinetics in the last five years. The diversity of reaction systems investigated and techniques used is indicative of the fact that chemi-ionization continues to be of interest to a number of not closely related disciplines. It is hoped that by collecting and comparing the information here, knowledge from several of these areas will have been made more useful for workers in other areas.

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## REFERENCES

- <sup>1</sup> A. Fontijn, *Progress in Reaction Kinetics*, **6**, 75 (1972) [also appeared separately as Vol. 6, Part 2 (1971)]. (a) Section II. (b) Section III. (c) Section IV.
- <sup>2</sup> F. W. Lampe in *Ion-Molecule Reactions*, Vol. 2, Chapter 13, J. L. Franklin, Ed. Plenum: New York (1972).
- <sup>3</sup> Y. A. Bush, D. L. Albritton, F. C. Fehsenfeld, A. L. Schmeltekopf, B. Brutschy and A. Niehaus, *J. Chem. Phys.* **57**, 4501 (1972).
- <sup>4</sup> R. S. Berry in *Proceedings of the International School of Physics, 'Enrico Fermi', Course 44'*, p. 193. Ch. Schlier, Ed. Academic Press: New York (1970).
- <sup>5</sup> R. D. Rundel and R. F. Stebbings in *Case Studies in Atomic Collision Physics*, Vol. II, Chapter 8. E. W. McDaniel and M. R. C. McDowell, Eds. North-Holland: Amsterdam (1972).
- <sup>6</sup> Z. Herman and V. Cermak, *Coll. Czech. Chem. Commun.* **31**, 649 (1966).
- <sup>7</sup> H. Hotop and A. Niehaus, *Z. Phys.* **228**, 68 (1969).
- <sup>8</sup> H. Hotop and A. Niehaus, *Z. Phys.* **238**, 452 (1970).
- <sup>9</sup> S. Wexler, 'Associative and non-associative ion pair formation by fast atoms', *Ber. Bunsenges. Phys. Chem.*, **77**, 606 (1973).
- <sup>10</sup> W. J. Miller in *Fourteenth Symposium (International) on Combustion*, p 307. The Combustion Institute: Pittsburgh (1973).
- <sup>11</sup> H. F. Calcote in *Ion-Molecule Reactions*, Vol 2, Chapter 15. J. L. Franklin, Ed. Plenum: New York (1972).
- <sup>12</sup> H. F. Calcote and W. J. Miller in *Reactions under Plasma Conditions*, Vol. 2, Chapter 17. M. Venugopalan, Ed. Wiley-Interscience: New York (1971).
- <sup>13</sup> J. Peeters, C. Vinckier and A. van Tiggelen, *Oxidation and Combustion Rev.* **4**, 1 (1969).
- <sup>14</sup> D. H. Stedman and D. W. Setser, *Progress in Reaction Kinetics*, **6**, 193 (1972).
- <sup>15</sup> W. H. Miller, *J. Chem. Phys.* **52**, 3563 (1970).
- <sup>16</sup> W. H. Miller and H. F. Schaefer, *J. Chem. Phys.* **53**, 1421 (1970).
- <sup>17</sup> W. H. Miller, C. A. Slocomb and H. F. Schaefer, *J. Chem. Phys.* **56**, 1347 (1972).
- <sup>18</sup> D. A. Micha, S. Y. Tang and E. E. Muschlitz, *Chem. Phys. Letters*, **8**, 587 (1971).
- <sup>19</sup> R. E. Olson, *Chem. Phys. Letters*, **13**, 307 (1972).
- <sup>20</sup> J. S. Cohen and N. F. Lane, *J. Phys. B: Atom. Molec. Phys.* **6**, L113 (1973).
- <sup>21</sup> G. H. Myers and H. W. Young, *J. Chem. Phys.* **51**, 1597 (1969).
- <sup>22</sup> D. E. Jensen, *Combust. Flame*, **12**, 261 (1968).
- <sup>23</sup> J. B. Mann, *J. Chem. Phys.* **40**, 1632 (1964).
- <sup>24</sup> *JANAF Thermochemical Tables*, 2nd ed., D. R. Stull, H. Prophet, Eds., National Bureau of Standards NBS-NSRDS-37, US Government Printing Office: Washington, DC (1971).
- <sup>25</sup> G. DeMaria, R. P. Burns, J. Drowart and M. G. Inghram, *J. Chem. Phys.* **32**, 1373 (1960).
- <sup>26</sup> H. Y. Wu and P. G. Wahlbeck, *J. Chem. Phys.* **56**, 4534 (1972).
- <sup>27</sup> W. L. Fite and P. Irving, *J. Chem. Phys.* **56**, 4227 (1972).
- <sup>28</sup> W. L. Fite, H.-H. Lo and P. Irving, Extranuclear Laboratories, Inc., Pittsburgh, private communication (1973).
- <sup>29</sup> P. Zavitsanos, GE Space Sciences Laboratory, King of Prussia, PA, *J. Chem. Phys.*, **59**, 2162 (1973) and private communication (1973).
- <sup>30</sup> W. L. Fite and B. Kim, University of Pittsburgh, private communication (1973).
- <sup>31</sup> R. Johnsen and M. A. Biondi, *J. Chem. Phys.* **57**, 1975 (1972).
- <sup>32</sup> R. Kelly and P. J. Padley, *Trans. Faraday Soc.* **67**, 1384 (1971).
- <sup>33</sup> D. E. Jensen, *J. Chem. Phys.* **51**, 4674 (1969).
- <sup>34</sup> A. N. Hayhurst and D. B. Kittelson, *J.C.S. Chem. Commun.* 422 (1972).
- <sup>35</sup> R. H. Neynaber, B. F. Myers and S. M. Trujillo, *Phys. Rev.* **180**, 139 (1969).
- <sup>36</sup> R. B. Cohen, C. E. Young and S. Wexler, *Chem. Phys. Letters*, **19**, 99 (1973).
- <sup>37</sup> R. B. Cohen, Illinois Institute of Technology, private communication (1973).
- <sup>38</sup> S. Matsuda and D. Gutman, *J. Chem. Phys.* **54**, 453 (1971); **53**, 3324 (1970).

- <sup>39</sup> M. C. Cavenor, G. Munday and A. R. Ubbelohde, *Combust. Flame*, **18**, 99 (1972).
- <sup>40</sup> M. A. Haney and J. L. Franklin, *Trans. Faraday Soc.* **65**, 1794 (1969).
- <sup>41</sup> W. A. Chupka, Argonne National Laboratory, private communication (1973).
- <sup>42</sup> N. Jonathan, A. Morris, M. Okuda and D. J. Smith, *J. Chem. Phys.* **55**, 3046 (1971).
- <sup>43</sup> R. R. Burke, *J. Chem. Phys.* **52**, 2164 (1970).
- <sup>44</sup> J. N. Bradley and R. S. Tse, *J. Chem. Phys.* **49**, 1968 (1968).
- <sup>45</sup> K. D. Bayes, *J. Chem. Phys.* **52**, 1093 (1970).
- <sup>46</sup> K. D. Bayes, UCLA, R. A. Young, York University, Toronto and J. E. Johnson, Naval Research Laboratory, Washington, DC, private communications (1972 and 1973).
- <sup>47</sup> M. MacGregor and R. S. Berry, *J. Phys. B: Atom. Molec. Phys.* **6**, 181 (1973).
- <sup>48</sup> A. Dalgarno, M. Oppenheimer and R. S. Berry, *Astrophys. J.* **183**, L21 (1973).
- <sup>49</sup> K. N. Bascombe, J. A. Green and T. M. Sugden in *Advances in Mass Spectrometry*, Vol. 2, p 66. R. M. Elliott, Ed., Pergamon: London (1963).
- <sup>50</sup> W. J. Miller, *Oxidation and Combustion Rev.* **3**, 97 (1968).
- <sup>51</sup> J. A. Green and T. M. Sugden in *Ninth Symposium (International) on Combustion*, p 607. Academic Press: New York, (1963).
- <sup>52</sup> A. N. Hayhurst and N. R. Telford, *Nature Phys. Sci.* **235**, 114 (1972).
- <sup>53</sup> A. van Tiggelen, J. Peeters and C. Vinckier in *Thirteenth Symposium (International) on Combustion*, p 311. The Combustion Institute: Pittsburgh (1971).
- <sup>54</sup> E. M. Bulewicz, P. J. Padley and R. E. Smith in *Fourteenth Symposium (International) on Combustion*, p 329. The Combustion Institute: Pittsburgh (1973).
- <sup>55</sup> H. F. Wellenstein and W. W. Robertson, *J. Chem. Phys.* **56**, 1077 (1972).
- <sup>56</sup> C. B. Collins, B. W. Johnson and M. J. Shaw, *J. Chem. Phys.* **57**, 5310 (1972).
- <sup>57</sup> J. J. DeCorpo and F. W. Lampe, *J. Chem. Phys.* **51**, 943 (1969).
- <sup>58</sup> N. T. Holcombe and F. W. Lampe, *J. Chem. Phys.* **57**, 449 (1972).
- <sup>59</sup> J. O. Hirschfelder and M. A. Eliason, *Ann. NY Acad. Sci.* **67**, 451 (1957).
- <sup>60</sup> V. Cermak, *J. Chem. Phys.* **44**, 3781 (1966).
- <sup>61</sup> V. Cermak and Z. Herman, *Chem. Phys. Letters*, **2**, 359 (1968).
- <sup>62</sup> V. Cermak, *Coll. Czech. Chem. Commun.* **33**, 2739 (1968).
- <sup>63</sup> H. Hotop, A. Niehaus and A. L. Schmeltekopf, *Z. Phys.* **229**, 1 (1969).
- <sup>64</sup> H. L. Kramer, J. A. Herce and E. E. Muschlitz, *J. Chem. Phys.* **56**, 4166 (1972).
- <sup>65</sup> M. S. B. Munson, J. L. Franklin and F. H. Field, *J. Phys. Chem.* **67**, 1542 (1963).
- <sup>66</sup> S. Y. Tang, A. B. Marcus and E. E. Muschlitz, *J. Chem. Phys.* **56**, 566 (1972).
- <sup>67</sup> M. Cher and C. S. Hollingsworth, *J. Chem. Phys.* **50**, 4942 (1969).
- <sup>68</sup> J. S. Howard, J. P. Riola, R. D. Rundel and R. F. Stebbings, *J. Phys. B: Atom. Molec. Phys.* **6**, L109 (1973).
- <sup>69</sup> H. Hotop and A. Niehaus, *Z. Phys.* **215**, 395 (1968).
- <sup>70</sup> H. Hotop and A. Niehaus, *Chem. Phys. Letters*, **3**, 687 (1969).
- <sup>71</sup> W. C. Richardson, D. W. Setser, D. L. Albritton and A. L. Schmeltekopf, *Chem. Phys. Letters*, **12**, 349 (1971).
- <sup>72</sup> W. C. Richardson and D. W. Setser, *J. Chem. Phys.* **58**, 1809 (1973).
- <sup>73</sup> Y. A. Bush, M. McFarland, D. L. Albritton and A. L. Schmeltekopf, *J. Chem. Phys.* **58**, 4020 (1973).
- <sup>74</sup> R. H. Neynaber, G. D. Magnuson and J. K. Layton, *J. Chem. Phys.* **57**, 5128 (1972); see also J. A. Rutherford and D. A. Vroom, *J. Chem. Phys.* **58**, 4076 (1973).
- <sup>75</sup> A. L. Schmeltekopf and F. C. Fehsenfeld, *J. Chem. Phys.* **53**, 3173 (1970).
- <sup>76</sup> J. R. Penton and E. E. Muschlitz, *J. Chem. Phys.* **49**, 5083 (1968).
- <sup>77</sup> C. Rebeck and J. Dubrin, *J. Chem. Phys.* **55**, 5825 (1971).
- <sup>78</sup> N. T. Holcombe and F. W. Lampe, *J. Chem. Phys.* **56**, 1127 (1972).
- <sup>79</sup> Z. Herman and V. Cermak, *Coll. Czech. Chem. Commun.* **33**, 468 (1968).
- <sup>80</sup> E. G. Jones and A. G. Harrison, *Int. J. Mass Spectrom. Ion Phys.* **5**, 137 (1970).
- <sup>81</sup> R. C. Bolden, R. S. Hemsworth, M. J. Shaw and N. D. Twiddy, *J. Phys. B: Atom. Molec. Phys.* **3**, 61 (1970).
- <sup>82</sup> W. A. Chupka, M. E. Russell and K. Refaye, *J. Chem. Phys.* **48**, 1518 (1968).
- <sup>83</sup> F. J. Comes and U. Wenning, *Z. Naturforsch.* **24a**, 1227 (1969).
- <sup>84</sup> M. J. Linevsky, GE Space Sciences Laboratory, King of Prussia, PA, unpublished data.
- <sup>85</sup> D. H. Klosterboer, Kansas State University, unpublished data.
- <sup>86</sup> H. Hotop, F. W. Lampe and A. Niehaus, *J. Chem. Phys.* **51**, 593 (1969).
- <sup>87</sup> U. Lauterbach, *Z. Naturforsch.* **23a**, 1790 (1968).
- <sup>88</sup> H. Hotop, *Diplom-Thesis*, Albert Ludwigs Universität, Freiburg, Germany (1967).