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Dissociative Ionization of CO by Ion Impact*

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Cross sections for the reactions $He^+ + CO \rightarrow C^+ + O + He$, $Ne^+ + CO \rightarrow C^+ + O + Ne$, and $Ar^+ + CO \rightarrow C^+ + O + Ar$ are studied as functions of ion kinetic energy. The first reaction exhibits the behavior expected for an exothermic reaction. The latter two prove to be endothermic and to have onsets which are surprisingly sharp. The experimental thresholds are in good agreement with values calculated from the well-accepted $D(CO) = 11.11$ eV. It appears that the technique used may prove to be useful for determining unknown bond-dissociation energies.

INTRODUCTION

THE bond-dissociation energy of CO and the related quantity, the heat of vaporization of carbon were, up to recent years, subjects of a long controversy.[1] After several decisive experiments,[2–4] there is now general agreement that $D(CO) = 11.11$ eV and $L(C) = 170$ kcal/mole. A few pieces of evidence remain, however, which are not in accord with the new measurements.

In particular, the work of Lindholm[5,6] on the dissociative ionization of CO by ion impact would seem to favor $D(CO) = 9.61$ eV. Lindholm uses an apparatus in which a primary ion beam selected by one mass spectrometer crosses a reaction chamber. Reaction products are extracted from the chamber at right angles to the primary ion direction, and analyzed by a second mass spectrometer. This second mass spectrometer is arranged to discriminate against secondary ions which acquire appreciable forward momentum in the interaction. Further, Lindholm believes it to be improbable that the kinetic energy of the low-energy primary ion enters into the energetics of reactions of the class he studies. He thus concludes that for any reaction which he detects with fairly large observed cross section, the energy imparted to the target molecule in the interaction equals the recombination energy of the primary ion used.

Lindholm observes the reaction $Ne^+ + CO \rightarrow C^+ + O + Ne$ and believes it to be induced by charge exchange. Thus, the semiquantitative theory of Massey and Burhop[7] should apply. Their predictions for nonresonant charge exchange are that the maximum cross section should occur for the ion velocity

$$v_m = a \mid \Delta E \mid / h, \tag{1}$$

and that for $v \ll v_m$ the cross section should have the form:

$$\sigma \propto \exp(-a \mid \Delta E \mid / 4hv), \tag{2}$$

where a is a length found empirically to be about 7×10^{-8} cm in typical cases and ΔE is the recombination energy of the primary ion minus the energy required to produce the particular state of the secondary ion involved. Using well-known ionization potentials,[8] one may readily calculate that for $D(CO) = 9.61$ eV, $\Delta E = +0.68$ or $+0.78$ eV, while for $D(CO) = 11.11$ eV, $\Delta E = -0.82$ or -0.72 eV. The former number in each case is for recombination of the $^2P_{\frac{3}{2}}$ state, the latter for the $^2P_{\frac{1}{2}}$ state. Experimentally, Lindholm measures a cross section for this reaction which is fairly large and which increases with decreasing ion kinetic energy, down to 25 eV. If $\Delta E = -0.72$ eV, one would predict a cross section which is very small at low energies and which reaches a maximum at about 3000 eV. Lindholm thus concludes that ΔE must be positive; takes the charge exchange to be a resonance or near-resonance process to a state of CO^+ excited beyond the dissociation limit, the excess energy coming off as kinetic energy of the C^+ and O fragments; and concludes that $D(CO) = 9.61$ eV.

In Lindholm's later paper,[6] published after it had become clear that $D(CO) = 11.11$ eV, he finds that new measurements have not resolved the difficulty. He concludes that Eqs. (1) and (2) are not applicable to this case and that the cross section must exhibit a decrease below the minimum energy obtained in his studies. The measurements reported here were made in an attempt to resolve this difficulty.

MEASUREMENTS

The measurements in the present report were made with the double mass spectrometer which has been described.[9] Because C^+ ions were produced with a distribution of kinetic energies in the ion source of the source mass spectrometer, there was a rather large

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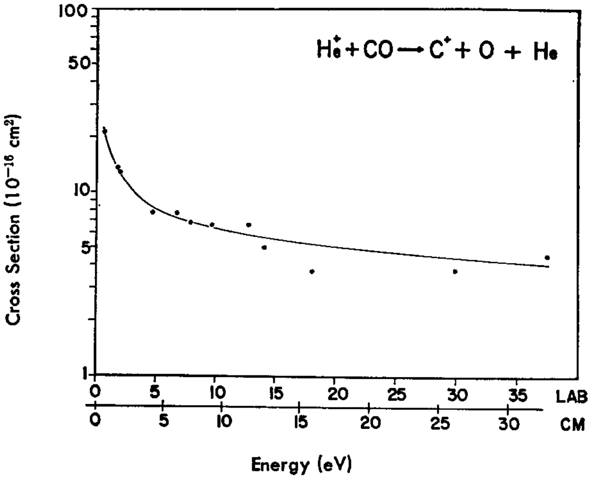

FIG. 1. Cross section for the reaction $He^+ + CO \rightarrow C^+ + O + He$ as a function of He^+ ion kinetic energy. Two energy scales are given, the upper scale for laboratory energy, the lower for energy in the center-of-mass system.

background of C^+ which leaked through this mass spectrometer when it was tuned to Ne^+ ions, particularly at low accelerating voltages. For this reason, it was necessary to obtain the Ne^+ ions of low kinetic energy by retardation from initial energies of 6 to 12 eV. Further, to obtain Ar^+ kinetic energies greater than 20 eV, it was necessary to accelerate the ions after analysis in the source mass spectrometer. In cases where it was possible to cross check a result by obtaining the same kinetic energy both with and without retardation and acceleration, the agreement was adequate.

DISCUSSION OF RESULTS

Measured cross sections for the reactions $He^+ + CO \rightarrow C^+ + O + He$, $Ne^+ + CO \rightarrow C^+ + O + Ne$, and $Ar^+ + CO \rightarrow C^+ + O + Ar$ are given as functions of primary ion kinetic energy in Figs. 1–3. To exhibit best the interesting onsets of these cross sections, the results are presented in semilogarithmic plots.

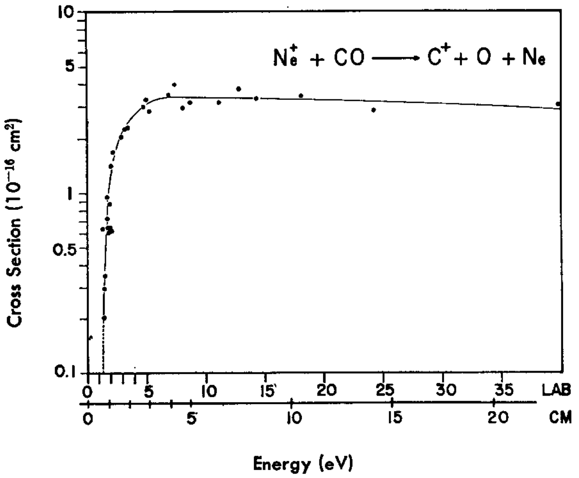

FIG. 2. Cross section for the reaction $Ne^+ + CO \rightarrow C^+ + O + Ne$ as a function of Ne^+ ion kinetic energy. Two energy scales are given, the upper scale for laboratory energy, the lower for energy in the center-of-mass system.

The reaction $He^+ + CO \rightarrow C^+ + O + He$ is definitely exothermic, ΔE being $+2.21$ eV for $D(CO) = 11.11$ eV. Thus, one expects no threshold behavior, and, indeed, the cross section (Fig. 1) increases as the ion kinetic energy is reduced, down to the lowest energy (0.6 eV) obtained.

The reaction $Ne^+ + CO \rightarrow C^+ + O + Ne$ is endothermic, with $\Delta E = -0.72$ eV. This means that *regardless of the detailed mechanism assumed for the reaction* the reaction cannot occur below a laboratory ion kinetic energy of E_{lab}, where

$$E_{lab} = 0.72 \text{ (total mass/target mass)} = 1.23 \text{ eV}.$$

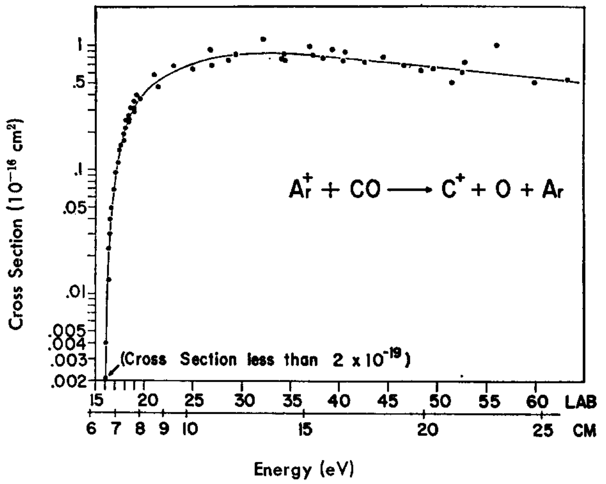

FIG. 3. Cross section for the reaction $Ar^+ + CO \rightarrow C^+ + O + Ar$ as a function of Ar^+ ion kinetic energy. Two energy scales are given, the upper scale for laboratory energy, the lower for energy in the center-of-mass system.

We see from Fig. 2 that the cross section does drop off sharply below an ion kinetic energy of 5 eV. Since, at present, we have no theory to provide a guide to the proper technique for establishing a threshold energy, it is dangerous to take the onset energy seriously. A vertical line through the steep portion of the curve cuts the energy axis at 1.3±0.1 eV, in good agreement with the threshold energy above.

Another endothermic process is $Ar^+ + CO \rightarrow C^+ + O + Ar$, for which $\Delta E = -6.62$ eV for the $^2P_{\frac{3}{2}}$ state of Ar^+, and -6.44 eV for the $^2P_{\frac{1}{2}}$ state.[8] The laboratory threshold energy should be 6.44 (68/28) = 15.65 eV. Figure 3 shows that the cross section for this reaction drops off at low energies. Again, one presently has no guide to the proper means for establishing a threshold, but the steep portion of the curve cuts the axis at 16.0 eV, and it appears that any reasonable criterion for picking a threshold will give a result within 0.5 eV of this value.

TABLE I. Comparison of present cross sections with cross sections of Lindholm.[a]

Reaction	Energy	Present results (10^{-16} cm^2)	Lindholm (10^{-16} cm^2)	Ratio	γ
$He^+ + CO \to C^+ + O + He$	25 eV	4.7	1.7	0.36	0.379
$Ne^+ + CO \to C^+ + O + Ne$	25 eV	3.0	0.8	0.26	0.806
$Ar^+ + CO \to C^+ + O + Ar$	50 eV	0.65	0.06	0.093	1.04

[a] See reference 6.

The onset of the reaction involving Ar^+ is not as sharp in terms of laboratory energy as for the reaction with Ne^+; however, in terms of energy in the center-of-mass system, they are more comparable, the reaction reaching full development in about 2.5 eV in the case of the Ne^+ reaction and in about 5 eV in the case of the Ar^+ reaction. Part of the difference is certainly the spread in ion energy from the small mass spectrometer. The effect of this energy spread is impossible to assess quantitatively because the distribution of ions with energy is not well known, but we believe the size of the effect to be no more than a few tenths of an electron volt. A further cause for differences in the threshold behavior for these reactions lies in the fact that the ion beam is a mixture of two states separated by 0.097 eV for Ne^+ and 0.178 eV for Ar^+. These two causes account only for a small portion of the smearing out of the onset; the remainder must be attributed to the characteristics of the reaction. Very possibly the form of the cross-section curve just above threshold is governed by available phase space as a function of excess energy.

The detailed nature of the reactions studied here is not clear. It is not possible, at present, to tell whether the reaction proceeds by formation of an excited CO^+ ion through charge transfer, followed by dissociation, or by a direct interaction of the three atoms followed by a separation of the three particles. It may be possible to investigate the mechanism by which the reaction proceeds by studying the cross sections for the formation of CO^+ and O^+.

The discussion in Ref. 9 of the uncertainties involved in the results applies here, also, except that in calculating the present results, the K_2 of this earlier report was always set equal to unity. We have no reliable information as to the value which K_2 actually assumes, but rough estimates—see below, Fig. 3 in Ref. 9, and Table I—indicate that K_2 is probably not a strongly varying function of energy over the energy ranges for which we have data. For the endothermic reactions presented here, K_2 might be as large as two for the higher energies and somewhat smaller than unity for points nearest the thresholds. For the reaction $He^+ + CO \to C^+ + O + He$, K_2 could conceivably be 4 or so and would increase at lower energies. Thus, the cross sections given here may be in error by a rather sizeable multiplicative factor, but the relative energy dependence should not be greatly different from that of the true, total cross sections.

In comparing the present results with those of Lindholm,[6] one must keep in mind that the experiments are quite different. The present experiment differs from Lindholm's in that there is no discrimination against processes in which substantial momentum is transferred from the primary to the secondary ion. Obviously, if a reaction is endothermic and requires that the kinetic energy of the primary ion be utilized, the products, neutral and charged, must acquire momentum in the forward direction. Table I compares the present cross sections with those of Lindholm.[6] Lindholm's results correspond to the differential cross sections integrated over some effective solid angle centered around 90° to the primary ion direction in the laboratory system, while our values correspond to an integration over a fairly large solid angle centered around 0°. Thus, one expects that if the reactions studied are really the same, Lindholm's values should be smaller than the present results. At present, it is not possible to predict what the ratio of Lindholm's cross sections to those given here should be because one knows neither the solid angle of acceptance of Lindholm's apparatus nor how to treat the complicated three-body separation, but the following very crude analysis may be of some value. If we assume that the excess energy in the center-of-mass system is shared equally among the three particles, we can calculate the ratio γ of the speed of the center of mass in the laboratory to the speed of the C^+ ion in the barycentric system. Values of γ are given in Table I. The larger the value of γ, the more the C^+ ions tend to be distributed in the original direction of the primary ion, which explains, qualitatively, the variation in the ratio of Lindholm's cross sections to those presented in this paper.

CONCLUSIONS

As a result of the present experiment a number of conclusions can be drawn:

(1) The difficulty of relating Lindholm's[6] results to the well-accepted bond energy of CO is now resolved.

(2) Lindholm's apparatus does not appear to discriminate very effectively against processes in which momentum is transferred to the secondary ion.

(3) It would appear to be quite risky to assume, as has been the practice, that the total energy given to the target system equals the recombination energy of the projectile ion, independent of its kinetic energy.[10]

(4) The efficiency of processes of the type studied here, in which kinetic energy of the projectile particle is utilized, is surprisingly high, and is worthy of some theoretical treatment.

(5) If the method used in the present report proves to have any generality, it appears that it is a technique capable of measuring dissociation energies with an accuracy, perhaps, of 0.1 eV.

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On the Optimum Use of Ionization-Efficiency Data

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The electron energy spread causes much fine detail in ionization efficiency curves to be obscured. The reduction of this spread by electron velocity analyzers is experimentally quite difficult. The present paper examines whether it is possible to reduce the effect of the energy spread by any analytical method.

It is found that the problem is very similar to that of the detection of radar signals in noise, and that similar methods can be applied. It is shown that typical ionization efficiency data contain a very much greater amount of information than is generally believed. Methods are developed for obtaining a marked reduction in the scatter in the experimental data and for reducing the effective electron energy spread by a factor of four or five times. The methods do not require an exact knowledge of the form of the electron energy spread, although the better this knowledge, the better the ultimate result.

Tests made on several artificial examples and on two actual cases show that the methods are of some promise. The results of this study also indicate a possible unconventional solution to the problem of achieving even higher resolution in energy in experimental ionization efficiency curves.

INTRODUCTION

WHEN molecules are subjected to bombardment in a mass spectrometer by a beam of electrons of controlled energy, positive ions may be formed. The probabilities of these ionization processes as functions of the electron energy would be expected to be characterized by a sharp onset at the ionization threshold. In all actual experiments, the electron beams used to produce the ionization are not monoenergetic, but contain a spread in energies. This spread has the effect of smearing out any sharp features of the ionization probability curves. The efficiency of production of a given ionic species, as a function of electron energy, is given, to a first approximation at least, by the sum of the probability curves for the production of that ion in each of its electronic states. Where the separation in energy of these states is less than the half-width of the electron energy distribution they cannot be resolved by inspection of the curves.

It has always been assumed that the only solution to the problem of increasing the resolution of the structure in these curves is to reduce the electron energy spread, and much effort has been devoted to this end.[1–5] The most successful approaches have been those in which a narrow slice is taken out of the initial energy distribution, and this is then used to produce the ionization. Reducing the energy spread in this way is difficult enough in itself, but also, the narrower the slice, the smaller the electron current obtainable, and therefore the worse the signal-to-noise ratio in the final data.

Various attempts have been made by the author,[6,7] and probably by many others in the past, to remove the energy spread by analytical methods. In practice, these have always failed because of the inevitable scatter in the individual experimental observations which made up the ionization-efficiency curves. Any attempt to remove the energy spread analytically

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