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Transient Species Produced by the Catalytic Decomposition of Acetone in a Mass Spectrometer*

CHARLES E. MELTON

From the Chemistry Division Oak Ridge National Laboratory, Oak Ridge, Tennessee

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The catalytic decomposition of acetone over Pt has been studied in a research mass spectrometer over the pressure range of from 10^{-2} to 1 Torr and over the temperature range of from 273° to 1673°K. Two negative ions, CH_3^- and $CH_3COCH_2^-$, and two free radicals, CH_3 and CH_3COCH_2, were observed in high concentrations in the gas phase during the course of the decomposition reaction. The principal stable products observed were CO and CH_4. This investigation shows that the CH_3^- ion reacts with acetone to produce CH_4. As far as can be judged from the experimental data, the $CH_3COCH_2^-$ is not involved in the main decomposition reaction, but rather is formed by surface ionization of the corresponding free radical.

Each of the free radicals appeared to be produced by a different elementary reaction. CH_3 probably resulted from the initial decomposition reaction on the surface, whereas CH_3COCH_2 was formed by a subsequent reaction of CH_3 with acetone.

By generalizing from the data collected, the first two steps in the decomposition reaction are specified. On this basis, CO is proposed to result from the first step of the reaction which involves one acetone molecule. Attention is drawn to the fact that in this system free radicals and negative ions can lead to the same stable products.

The decomposition reaction is heterogeneous because the observed activation energy of 34.4 kcal/mole of acetone is about one-half of that required for the homogeneous reaction. The present results are not inconsistent with a free radical chain mechanism for the homogeneous decomposition of acetone.

An attempt is made to estimate the conditions under which appreciable concentrations of ions on catalytic surfaces might be expected. This is done by treating a typical catalytic reaction from a point of view of the energetics involved.

INTRODUCTION

Although the decomposition of acetone by various means has been studied extensively for many years (*1–9*), comparatively little work has been done to identify the transient species involved in the reaction. Early studies of acetone decomposition by Hinshelwood and co-workers (*1, 3, 5*) suggested that the homogeneous decomposition involved a unimolecular process because of the first order rate law. Rice and co-workers (*2, 4*), on the other hand, presented evidence that the reaction involved a free radical chain mechanism, but the details of this proposed chain reaction differed considerably (*3, 5*) from other less ambiguous chain reactions. The controversy continued until 1944 when Smith and Hinshelwood carefully reexamined the reaction mechanism and concluded from radical scavenger studies that the reaction did probably follow a free radical chain mechanism. More recent studies (*7, 9, 10*) tend to confirm the free radical chain mechanism.

Since, in its simplest form, the mass spectrometer is really a combined reaction chamber and analytical tool, transient species as well as final products can be identified and quantitatively measured during the course of a chemical reaction. Al-

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though the mass spectrometer affords a formal method of associating certain observed transient species with possible species on the surface, it does not, in itself, give any direct method of finding just what species are on the surface or how the observed species enter into the reaction. To make any quantitative progress in identifying the elementary reactions involved, it is necessary to either make certain assumptions on the basis of the identity of the transient species or to add certain foreign substances to change the character of the reaction. The results, properly interpreted, should give much insight into the nature of the elementary reactions.

The mass spectrometer has often been used in connection with heterogeneous and homogeneous decomposition studies (*11*, *12*). However, previous studies suffered from the basic limitation that the pressure in the reaction chamber could not exceed about 10^{-4} Torr. Furthermore, since both the nature and concentration of transient species are inevitably sensitive to pressure, it is imperative to remove this basic limitation to be reasonably sure that most gas-phase transient species are identified. This limitation was largely removed by the advent of the high-pressure mass spectrometer which was utilized to identify transient species evolving from a hot catalyst at pressures of the order of 1 Torr (*13*, *14*, *15*).

We do not wish to imply in this discussion that previous results obtained at low pressure are not useful. On the contrary, much insight into the elementary steps of catalytic reactions has been obtained from low-pressure studies combined with special techniques such as that of secondary ion emission developed by Fogel *et al.* (*16*, *17*).

Ideally, we could determine all of the steps in any chemical reaction if we had a means to identify the participating atoms or molecules during the entire course of the reaction. This ideal has never been fully realized and consequently the elementary steps of most chemical reactions are uncertain. The high-pressure spectrometer offers a good approximation to attaining this ideal. True, the time scale between formation and identification of a species is limited to about a microsecond in the mass spectrometer but the technique has not been fully exploited within this limitation. In this study, the same basic limitation prevents the observation of transient species with a lifetime of less than 10^{-6} sec.

We shall present results in the present paper from a detailed study of the catalytic decomposition of acetone over Pt. The method of attack is analogous to that of our previous study (*15*) for the decomposition of NH_3. The interpretation will, of necessity, be both inductive and deductive because of the lack of an exact knowledge of the species on the surface, but it should produce at least some features of the elementary reactions occurring during the course of the decomposition and also serve as a basis for future investigations.

EXPERIMENTAL

The techniques for producing and detecting transient species in this work were essentially the same as those described for the initial CO_2–D_2 study (*14*) and the subsequent NH_3 study (*15*). A sample of acetone from a large reservoir is passed into the ionization chamber or reaction chamber of a research mass spectrometer which contains a Pt catalyst with a surface area of approximately 1 cm^2. The pressure in the reaction chamber is continuously variable from 10^{-8} Torr to 1 Torr as measured by our standard techniques (*18*). A number of different techniques are available to detect and identify possible transient species, as noted in Table 1. To illustrate the table, let us suppose a transient species, AB, has a steady state gas-phase concentration of 10^9 molecules/cc, and is stable to both positive and negative ionization. We note in column 3 that the lower limit for detection is 10^6 molecules/cc for positive ionization and 10^8 ions/cc for negative ionization; thus, the species should be easily observed by either positive or negative ionization. Observation by surface ionization depends on the ionization potential and electron affinity, as will be shown later.

Gas-phase free radicals were identified by maintaining the energy of the ionizing electrons below that necessary to produce

TABLE 1

LOWER LIMIT FOR DETECTION BY MASS SPECTROMETRY OF TRANSIENT SPECIES FORMED DURING CHEMICAL REACTIONS

Mode of ionization	Lower limit for detection (concentration/cc)	Restrictions
Positive Ionization[a] $AB + e \rightarrow AB^+ + 2e$ $A + e \rightarrow A^+ + 2e$	10^6 molecules/cc	Stable to positive ionization Lifetime $> 10^{-6}$ sec
Negative Ionization $AB + e \rightarrow AB^-$ $\rightarrow A + B^-$ $\rightarrow A^+ + B^-$ $A + e \rightarrow A^-$	10^8 molecules/cc	Stable to negative ionization Lifetime $> 10^{-6}$ sec
Surface Ionization $A + S \rightarrow A^+ + S$ $B + S \rightarrow B^- + S$	10^4 molecules/cc	Low ionization potential or high electron affinity. Ion stable for $> 10^{-6}$ sec
	10^2 ions/cc for charged species, e.g., NH_4^+, CH_3^-	Ion stable for $> 10^{-6}$ sec

[a] Where AB is either a transient molecule or a final product and A and B are free radicals or atoms.

interfering fragment ions by dissociative ionization of either residual or reactant gases. Charged species evolving from the surface of the hot catalyst were identified by direct observation, i.e., without an ionizing electron beam.

The ratio of ions to neutrals evolving from a hot metal surface which is bombarded by neutral particles is given by the well-known Saha-Langmuir equations (*19*) (a brief résumé of these equations is given in the Appendix).

$$\frac{N^+}{N_0} = \frac{(1 - r_i)}{(1 - r_0)} \frac{\omega_i}{\omega_0} \exp\left(\frac{\phi - I}{kT}\right) \quad (1)$$

$$\frac{N^-}{N_0} = \frac{(1 - r_i)}{(1 - r_0)} \frac{\omega_i}{\omega_0} \exp\frac{(EA - \phi)}{(kT)} \quad (2)$$

The symbols are defined as

N^+/N_0; N^-/N_0	ratio of the charged to the neutral component leaving the surface
r_i, r_0	reflection coefficients of the surface for the ion and the neutral
ω_i and ω_0	statistical weighting factors for the ion and the neutral
I	ionization potential
EA	electron affinity
ϕ	electron work function of the metal
T	absolute temperature
k	Boltzman's constant

Although these equations are derived from first principles, they should be used with caution because of the effect (*20*) of different adsorbed materials on ϕ. Furthermore, the reflection coefficients for a given surface are usually unknown.

The absolute concentration of neutral transient species ionized by electron bombardment is estimated from the relationship (*20*)

$$[AB] = [AB^{\pm}]/\sigma N_e \ell \quad (3)$$

where N_e is the number of electrons, ℓ is the distance the electrons travel within the ionization chamber, essentially the "mean free path," σ is the cross section for ionization by electrons of a given energy, and $AB^{\pm}$ is the number of ions observed, either positive or negative. Usually σ is not known with any degree of accuracy, but the value is not very different for two similar compounds. Therefore, one can obtain a reasonable estimate of σ for a species such as CH_3 by measuring the value for a similar compound, for example CH_4. The comparison must be made for the same value of $|E - I|$, since σ for positive ionization changes approximately as the relationship (*21*)

$$\sigma \cong \sigma_0(E - I)$$

where E is the energy of the ionizing electrons, σ_0 is a proportionality constant, I is the ionization potential, and $|E - I|$ does not exceed about 10 eV.

RESULTS AND DISCUSSION

A. *Neutral Transient Species*

We now consider the results for neutral transient species observed in the gas phase during the decomposition reaction. The results for charged transient species are given later in Section B.

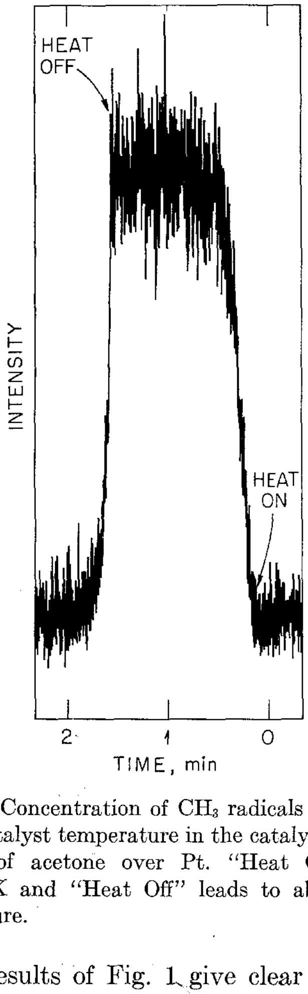


FIG. 1. Concentration of CH_3 radicals as a function of catalyst temperature in the catalytic decomposition of acetone over Pt. "Heat On" leads to 1373°K and "Heat Off" leads to about room temperature.

The results of Fig. 1 give clear evidence for the existence of a gas-phase transient species produced during the reaction. To obtain these results, the temperature of the catalyst was abruptly changed from room temperature to 1373°K while monitoring the CH_3^+ mass position using 10-eV ionizing electrons. An abrupt change in the catalyst temperature gave a corresponding abrupt change in the CH_3 concentration, thus demonstrating that the CH_3 evolves from the catalyst. Low-energy ionizing electrons were necessary in the experiment because high-energy electrons produce CH_3^+ by dissociative ionization of acetone, which is indistinguishable from the CH_3^+ resulting from primary ionization of CH_3 neutrals.

Other transient species were identified by scanning the mass spectrum in the range from mass 12 to mass 100 first with the catalyst cold and again with the catalyst hot and using 75-eV ionizing electrons. Any change in the intensity of a given ion or the appearance of a new ion in the two experiments was attributed to the difference in the temperature of the catalyst. Having made these tests, we estimated the concentration of each species of interest by substituting the measured values in Eq. (3). A summary of the results for all of the neutral species observed by these techniques is given in Table 2 together with the approximate concentration of each product and the postulated reactions. Evidence for the reaction mechanism given is obtained from the considerations which follow.

Let us first investigate the source of the CH_3 free radical which (from Table 2) has an abundance of 28% for a catalyst temperature of 1373°K, 3% acetone decomposition, and 0.5 Torr total partial pressure of acetone. There are only two probable sources of neutrals for the radical, either thermal decomposition of acetone in the gas phase or decomposition on the catalytic surface. We can easily distinguish between these two possibilities by determining the activation energy. For the gas-phase decomposition, the activation energy is in the range of 65–75 kcal (*1–6*), whereas that for the surface reaction is probably about one-half this value. Results obtained by temperature studies are shown in Fig. 2 and indicate that the activation energy is 34.3 kcal, clearly demonstrating that we are dealing with a surface reaction rather than a homogeneous decomposition reaction. Pressure studies of CH_3, Fig. 3, showed a first order rate de-

TABLE 2

RESULTS FROM THE DECOMPOSITION (3%) OF ACETONE AT 1373 K° AND A PRESSURE OF 0.5 TORR

Postulated reaction	Abundance of products[a] (%)		Evidence
(I) $CH_3COCH_3 \xrightarrow{S} 2CH_3 + CO$	CH_3 CO	(28) (26)	The low activation energy (34.4 kcal, Fig. 1) requires a surface reaction (80 kcal for the gas-phase reaction). Concentrations of CH_3 and CO obey a first order rate law
(II) $CH_3 + CH_3COCH_3 \rightarrow CH_4 + CH_3COCH_2$	CH_4 CH_3COCH_2	(23) (21)	The concentrations of CH_3COCH_2 and of CH_4 follow a second order rate law (Fig. 4)
(III) $CH_3COCH_2 \rightarrow CH_3 + COCH_2$	$COCH_2$ CH_3	(0.1) —	Postulated from low abundance of product
(IV) $CH_3 + CH_3 \rightarrow C_2H_6$	C_2H_6	(0.01)	Low abundance suggests radical–radical reaction
(V) $CH_3 + CH_3COCH_2 \rightarrow C_2H_5COCH_3$	$C_2H_5COCH_3$	(0.01)	Low abundance suggests radical–radical reaction

[a] Values given may be in error by a factor of 2.

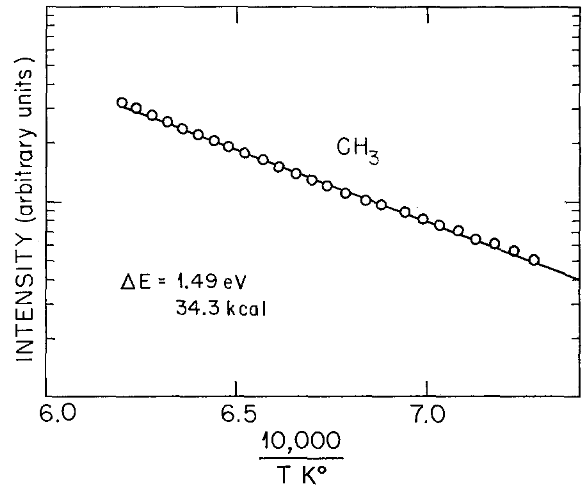


FIG. 2. Concentration of CH_3 radicals as a function of temperature in the catalytic decomposition of acetone over Pt.

pendence in accord with heterogeneous decomposition. These observations, together with the amount of CO observed, permit us to state with a high degree of certainty that the first step in the decomposition of acetone involves one molecule of acetone and is of the form

$$CH_3COCH_3 \xrightarrow{Pt} 2CH_3 + CO \qquad (I)$$

Reaction (I), as written, is about 80 kcal endothermic, whereas we observe an activation energy of 34.3 kcal. This requires enough of the products on the right to be chemisorbed to lower the energy of activation to 34.3 kcal.

We have not yet determined the role of CH_3 in the decomposition, but we have already determined that one final product, CO, is probably formed by the first step of the reaction. Pressure studies of CO showed

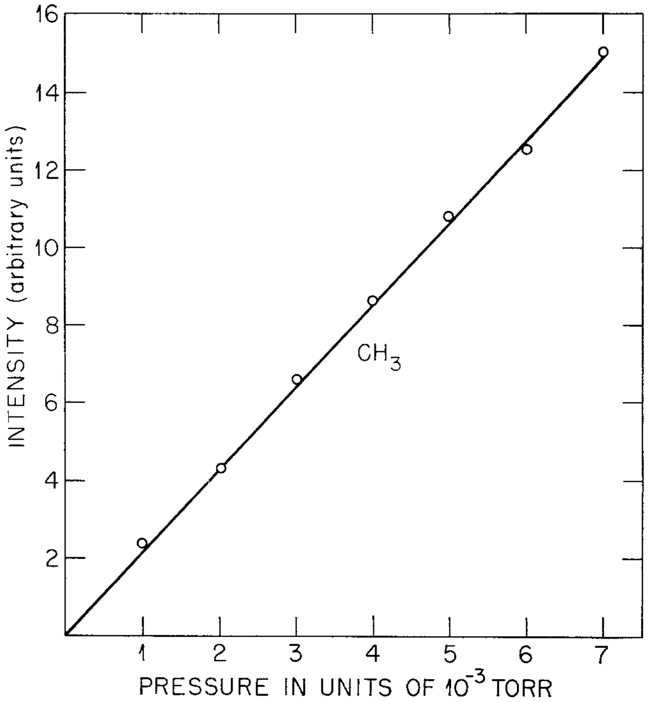


Fig. 3. Concentration of CH_3 radicals as a function of acetone pressure in the decomposition of acetone over Pt for a temperature of 1373°K.

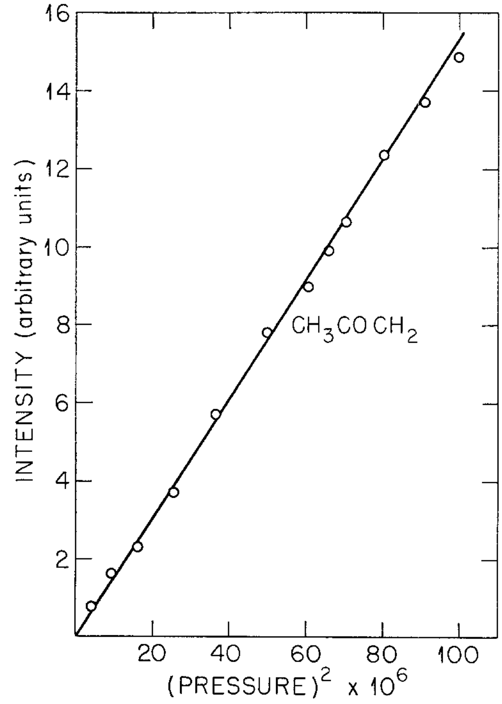


Fig. 4. Concentration of CH_3COCH_2 radicals as a function of acetone pressure squared in the decomposition of acetone over Pt.

a first order rate dependence which confirm reaction (I) as the initial step. The experimental apparatus used in this study did not have sufficient resolution to separate CO^+ and $C_2H_4^+$, another possible product, but isotopic and negative ion studies (*18*) showed that at least 95% of the mass 28 ion beam was due to CO^+.

As for the second step in the reactions, the results given in Fig. 4 show that the abundance of CH_3COCH_2 is proportional to the square of the pressure. The abundance of CH_4 was also second order with respect to pressure. Thus, a reaction of the form

$$CH_3 + CH_3COCH_3 \rightarrow CH_4 + CH_3COCH_2 \quad \text{(II)}$$

is indeed consistent with experimental observations. This hydrogen abstraction reaction (II) has been observed in the gas phase by other workers (*7*, *9*, *15*) using entirely different techniques. Dainton *et al.* (*7*) postulated reaction (II) from C^{14} labeling of CH_3 and Briton (*9*) obtained evidence for reaction (II) in high-temperature photolysis studies.

Reactions (III), (IV), and (V) of Table 2 are postulated from the composition of the products. It is not known whether the reactions occur on the surface or in the gas phase or both. A gas-phase mechanism to produce these products is in accord with the proposals of other workers (*2*, *7*, *9*) for a free radical chain sequence in the homogeneous decomposition of acetone.

B. Gas-Phase Ions

The existence of charged species in the gas phase during the decomposition reaction is shown by the striking results of Fig. 5. In this experiment the temperature of the catalyst was suddenly changed from room temperature to 1473°K while monitoring the CH_3^- ion beam with no ionizing electron beam present. The CH_3^- intensity increases and decreases abruptly, corresponding to abrupt changes in the catalyst temperature.

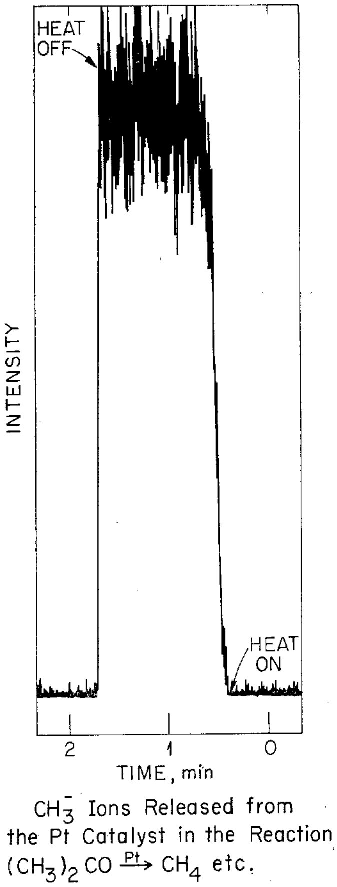


FIG. 5. Concentration of CH_3^- ions as a function of catalyst temperature in the decomposition of acetone over Pt. "Heat On" leads to 1473°K and "Heat Off" leads to about room temperature.

A similar study of the $CH_3COCH_2^-$ ion beam gave identical results. No other positive or negative ions were observed in the gas phase with the catalyst hot and the electron beam turned off.

If surface ionization is the source of the negative ions, the concentration of the corresponding free radicals in the gas phase can be estimated from Eq. (2). Results from such a calculation can then be compared to the actual concentration of the corresponding radicals determined by Eq. (3) to determine whether sufficient neutrals are present in the gas phase to account for the ions. Unfortunately, the concentration of CH_3COCH_2 cannot be determined explicitly from the $CH_3COCH_2^-$ intensity and Eq. (2) because the exact value of the electron affinity of CH_3COCH_2 is not available. A reasonable value of *EA* of 1.5 eV was assumed in making the calculations, which should give a rough estimate of the amount of CH_3COCH_2 necessary in the gas phase.

Results from the calculations are presented in Table 3 and are compared to the observed concentration of the free radicals. The calculation for $CH_3COCH_2^-$ was qualitative and limited to one temperature because we had to assume a value for the electron affinity of $CH_3COCH_2^-$.

TABLE 3

RESULTS FOR THE CONCENTRATION OF CH_3 AT VARIOUS TEMPERATURES AND A CONSTANT PARTIAL PRESSURE OF ACETONE OF 0.5 TORR

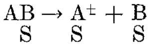
	Partial pressure of CH_3 (Torr)		
T (°K)	Calculated by Eq. (3)	Calculated by Eq. (2)	CH_3^- (ions/sec[a])
1373°	1.5×10^{-2}	1.3×10^{-2}	9.5×10^{3}
1473°	2.3×10^{-2}	1.8×10^{-2}	1.15×10^{5}
1573°	4.0×10^{-2}	3.8×10^{-2}	1.35×10^{6}
1673°	7.2×10^{-2}	6.2×10^{-2}	1.47×10^{7}
	Partial pressure of CH_3COCH_2[b]		$CH_3COCH_2^-$
1473°	1.9×10^{-2}	1.4×10^{-2}	1.6×10^{5}

[a] Area of catalyst, 1 cm^2.

[b] Depends on the pressure of both CH_3 and CH_3^-; see text.

General Conditions for Ionization by Catalytic Surfaces

We have presented evidence from the present study that the ionic species $CH_3COCH_2^-$ in the gas phase was formed by surface ionization of gas-phase free radicals rather than by displacement of adsorbed ions from the surface. On the other hand, the ionic species, NH_4^+, observed in the study (*11*) of the decomposition of NH_3 apparently did not result from surface ionization of gas-phase free radicals, but rather evolved directly from the catalytic surface, suggesting an appreciable concentration of adsorbed ions on the surface. Results from these two studies show, therefore, that the observation of ions in the gas phase during a catalytic reaction does not necessarily indicate a high concentration of adsorbed ionic species on the surface. Under what conditions can we expect appreciable ionization of reactants or intermediates during the course of a typical catalytic reaction?



$$\underset{S}{AB} \rightarrow \underset{S}{A^{\pm}} + \underset{S}{B}$$

A qualitative answer to this question is obtained by elementary thermochemical considerations in which ΔH for a given reaction is estimated. We need as parameters (1) the ionization potential (I), (2) the electron affinity (EA), (3) the heat of adsorption of an ion (E_a), (4) the energy of chemisorption (E_c), (5) the energy of physical adsorption (E_p), (6) the work function of the catalyst (ϕ), and (7) the dissociation energy (D) of the molecule of interest. For positive ionization ΔH is given by

$$\Delta H = E_p + D + I - \phi - \eta E_a - \eta E_c \quad (4)$$

where η refers to the number of species, and for negative ionization

$$\Delta H = E_p + D + \phi - EA - \eta E_a - \eta E_c \quad (5)$$

All of these parameters are either available or can be estimated.

The heat of adsorption of an ion E_a on any metal surface can be estimated by elementary physical principles. An ion adsorbed on a metal surface causes polarization of the surface and induces an equal but opposite charge within the surface, the so-called image charge. The attractive force, F, between the charge and the image charge constituting a dipole is given by Coulomb's law as

$$F = e^2/d^2 = e^2/(2r)^2 \quad (6)$$

where d is the length of the dipole and is equal to $2r$ for an ion on a surface where r is the radius of the ion. The energy, E, required to separate the two charges or to completely remove the ion from the surface is given by the expression

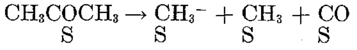
$$E_a = e^2/2r \quad (7)$$

Introducing the proper constants into Eq. (*7*) for expressing E_a in eV and r in angstroms, we have

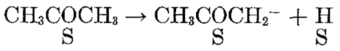
$$E_a = 3.60/r \quad \text{eV} \quad (8)$$

For a typical dissociation reaction where AB is any molecule, B is uncharged, and $A^{\pm}$ is either a positive or negative ion, Eqs. (4) and (5) show ΔH is negative (the reaction is exothermic) for either $I \leq 10$ eV or $EA \geq 0.6$ eV for a Pt surface with $\phi = 5$ eV. Thus, molecules with high ionization potentials and low electron affinities such as N and H are unlikely to reside on the surface as ions. These conclusions are consistent with those of Emmett and Teller (*22*) regarding ions on catalytic surfaces.

The general scheme for evaluating ΔH for ionization, utilizing Eqs. (4) and (5), can be applied to possible reactions of acetone which could explain the observed negative ions in the gas phase



$$\underset{S}{CH_3COCH_3} \rightarrow \underset{S}{CH_3^-} + \underset{S}{CH_3} + \underset{S}{CO} \quad (VI)$$



$$\underset{S}{CH_3COCH_3} \rightarrow \underset{S}{CH_3COCH_2^-} + \underset{S}{H} \quad (VII)$$

We find that reaction (VI) is exothermic by perhaps 1 eV and reaction (VII) is endothermic by at least 4 eV for typical values of $E_p = 0.2$, $D = 3.5$, $\phi = 5$, $EA = 1.5$, $E_a = 3.6$, and $E_c = 2$ eV. The CH_3^- ion may therefore be formed on the surface by dissociation and ionization of adsorbed acetone, whereas such a mechanism is unlikely for the formation of $CH_3COCH_2^-$.

Franck (*23*) has shown that some ions such as H^+ may be adsorbed more strongly than Eq. (8) predicts. Martin (*24*) has experimental evidence in accord with Franck's conclusions. Thus Eq. (8) should be regarded as a lower limit for the energy of adsorption for ions such as H^+.

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APPENDIX I

IONIZATION BY HOT METAL SURFACES

Let us consider the equilibrium between a gas and an incandescent metal surface. This means that atoms, ions, and electrons are continually emitted and adsorbed by the surface but the population of each in the gas phase is independent of time, or remains constant. To develop a relationship for the ratio of charged to neutral component leaving the surface, we consider the equilibrium of each species separately, starting with the electrons. We know from kinetic theory that the number of electrons per cm² per sec incident on the surface is given by the expression

$$N_a = \frac{N_e}{4}\bar{v} = \frac{N_e}{4}\left(\frac{8kT}{\pi m}\right)^{1/2} \qquad (7)$$

where $\bar{v}$ is the average velocity, N_e is the number of electrons per unit volume in the gas phase, and m is the mass of the electron. If we assume to a first approximation that all of the incident electrons are adsorbed, we can equate the number adsorbed, Eq. (7), to the number emitted per cm² per sec as given by Richardson's Eq. (8)

$$N = \frac{4\pi mk^2}{h^3} T^2 \exp -\left(\frac{\phi}{kT}\right) \qquad (8)$$

to obtain an expression for N_e

$$\frac{N_e}{4}\left(\frac{8kT}{\pi m}\right)^{1/2} = \frac{4\pi mk^2}{h^3} T^2 \exp -\left(\frac{\phi}{kT}\right)$$

$$N_e = 2\frac{(2\pi mkT)^{3/2}}{h^3} \exp -\left(\frac{\phi}{kT}\right) \qquad (9)$$

We now look for a relationship between ions, neutrals, and electrons in the gas phase. Such a relationship is given by the equilibrium constant K_e for the reaction

$$M \leftrightarrows M^+ + e$$

and the equilibrium constant may be expressed with reflection coefficients to include a surface as

$$K_e = \frac{N_i N_e}{N_0}\frac{(1-r_0)}{(1-r_i)} \qquad (10)$$

where N_i is the number of ions, N_0 is the number of neutrals, and r_i and r_0 are the reflection coefficients of the surface for ions and neutrals, respectively. Should all ions be adsorbed and reemitted by the surface, the reflection coefficient is zero and the surface does not change the equilibrium. We note that Eq. (9) is the translational partition function for electrons. We may express K_e in terms of partition functions also, to obtain from statistical mechanics

$$K_e = \frac{F_i F_e}{F_0} \exp -\left(\frac{I}{kT}\right) \qquad (11)$$

where F_i, F_e, and F_0 are the respective partition functions of the ion, electron, and atom (translational only for the monoatomic species) and I is the ionization potential. The appropriate partition functions are

$$F_e = \omega_e \frac{(2\pi mkT)^{3/2}}{h^3} \qquad (12)$$

$$F_i = \omega_i \frac{(2\pi M_i kT)^{3/2}}{h^3} \qquad (13)$$

$$F_0 = \omega_0 \frac{(2\pi M_0 kT)^{3/2}}{h^3} \qquad (14)$$

where the ω's refer to statistical weights. We now have one equilibrium constant in terms of partition functions, Eq. (11), and another in terms of the ratio of ions to neutrals, Eq. (10). We equate the two expressions and obtain

$$\frac{N_i N_e(1-r_0)}{N_0(1-r_i)} = \frac{\omega_i}{\omega_0}\frac{F_i F_e}{F_0} \exp -\left(\frac{I}{kT}\right) \qquad (15)$$

Since N_e, except for the Boltzman factor, in Eq. (9) equals F_e as given by Eq. (12), we may cancel these quantities and retain only the Boltzman factor. We obtain after rearranging terms and making the proper substitutions, the well-known Saha-Langmuir expression

$$\frac{N_i}{N_0} = \frac{(1 - r_i)}{(1 - r_0)} \frac{\omega_i}{\omega_0} \exp\left(\frac{\phi - I}{kT}\right) \qquad (1)$$

A similar treatment for negative ionization leads to Eq. (2) which contains *EA* in place of *I*.

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