



# The Photolysis of Acetic Anhydride

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Citation: The Journal of Chemical Physics **19**, 1250 (1951); doi: 10.1063/1.1748006 View online: http://dx.doi.org/10.1063/1.1748006 View Table of Contents: http://scitation.aip.org/content/aip/journal/jcp/19/10?ver=pdfcov Published by the AIP Publishing

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### The Photolysis of Acetic Anhydride\*

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The photolysis of acetic anhydride probably by 1849A radiation has been studied in the temperature range 80° to 300°C at pressures of 10–60 mm dibutyl phthalate. From 80° to 224°C the rate is first order during a run but the specific rate decreases with increasing pressure. The gaseous products are CO, CO<sub>2</sub> and C<sub>2</sub>H<sub>6</sub> in approximately equivalent amounts. Biacetyl and methyl acetate have been identified among the liquid products. At 300°C the reaction is more complex, yields considerable amounts of H<sub>2</sub> and CH<sub>4</sub> and is not first order. Comparison with formic acid photolysis leads to an approximate quantum yield of 2. A mechanism is suggested which accounts qualitatively for the observations. Deactivation of activated reactant molecules by acetic anhydride and by the gaseous products accounts for the low quantum yield. Added C<sub>2</sub>H<sub>6</sub> and CO<sub>2</sub> are shown to increase the rate of photolysis, the more so the lower the pressure of acetic anhydride. Preliminary experiments have shown that the reaction can also be mercury sensitized at a much faster rate at comparable temperatures but yielding the same products in similar amounts.

'HE anhydrides are the only family of simple organic compounds that has not been subjected to extensive photochemical study. Berthelot and Gaudechon<sup>1</sup> report an analysis of the gaseous products from acetic anhydride upon irradiation with ultraviolet light for many hours, as follows: 36 percent CO, 22 percent  $CO_2$ , 23 percent  $C_2H_6$ , and 19 percent  $CH_4$ . No other report on the photolysis of an acid anhydride appears in the literature due undoubtedly to the lack of absorption of light above 2000A.<sup>2</sup> The absorption spectrum of acetic anhydride vapor in the region of strong absorption has not been determined. By using a mercury resonance lamp emitting some 1849A radiation built inside the reaction vessel, sufficient intensity of the light absorbed by acetic anhydride vapor was obtained to bring about a reasonably rapid photolysis permitting a general survey of the kinetics of the decomposition.

#### EXPERIMENTAL

The reaction vessel was modeled after the design of Steacie and Phillips.<sup>3</sup> It consisted of a quartz spiral of 10 mm outside diameter tubing connected through graded seals to Pyrex tubing of the same diameter carrying the electrodes which were standard neon sign coated electrodes, 8 mm in diameter and 3 cm long. The Pyrex reaction vessel of about one liter capacity was ring sealed to the Pyrex tubing near the electrode chambers and carried an inlet and outlet tubing, as also a thermocouple well. The quartz tube contained a drop of mercury and neon at a pressure of 10 mm. The lamp was operated from a 5000-volt, 25-ma transformer. The starting potential was 5000 volts though the normal operating potential was only 400 volts. The lamp furnished large amounts of 2537A and small amounts of 1849A radiation. At full intensity the reaction vessel maintained a temperature of 40°C. The temperature was measured using a chromel-alumel thermocouple.

A second reaction vessel similar to the foregoing but using larger electrodes, with 10-mm argon in place of neon and operated from a 5000-volt, 120-ma transformer was used in the later runs reported. The primary of the transformer was actuated by a Sorenson voltage regulator at 115 volts. Larger amounts of 1849A radiation were afforded by this lamp as judged by the more rapid reaction produced. The operating voltage was again 400 but the temperature of the reaction vessel was 80°C. This vessel was enclosed in a cylindrical oven which permitted the electrodes to protrude so that they would not be heated when the reaction vessel was heated to 300°C.

The reaction vessel was connected to a mercury diffusion and oil pump system, a McLeod gauge, a mercury manometer, a dibutyl phthalate manometer, and a Toepler pump leading to freeze-out traps and a Burrell gas analyzer.

Acetic anhydride was distilled through a column packed with carbon rings and a fraction boiling between 139 and 140°C was collected in a dry vessel open to the air through a drying tube containing anhydrous calcium sulfate. This vessel was connected to the manifold of the reaction system and the anhydride was distilled in vacuum into a storage bulb in dry ice. The solid was pumped out for several hours, allowed to warm to room temperature, refrozen, and pumped out again, the process being repeated until no bubbles appeared in the liquid on melting and no residual gas remained on freezing the liquid.

The formic acid used to determine quantum yields was dried over anhydrous calcium sulfate, introduced into the system and treated in a manner similar to that used for the anhydride. Both chemicals were stored under their own vapor pressures at room temperature.

Experiments were made using the first reaction vessel by both dynamic and static methods. The effect of the presence of mercury vapor was also studied. For this

<sup>\*</sup> Abstract from a dissertation presented in partial fulfillment of the requirements for the degree of Doctor of Philosophy at New York University, February, 1950. <sup>1</sup> Berthelot and Gaudechon, Compt. rend. **151**, 478 (1910); **153**,

<sup>&</sup>lt;sup>1</sup>Berthelot and Gaudechon, Compt. rend. 151, 478 (1910); 153, 383 (1911).

<sup>&</sup>lt;sup>2</sup> Ley and Arends, Z. physik. Chem. **17B**, 177 (1932). <sup>8</sup> Stancie and Philling Can. I. Pesserah. **B16**, 210 (1038)

<sup>&</sup>lt;sup>8</sup> Steacie and Phillips, Can. J. Research, B16, 219 (1938).

the acetic anhydride vapor was bubbled first through mercury at 100°C and then through mercury at 40°C, the temperature in the reaction system. In the flow runs the system was evacuated thoroughly, the lamp was turned on and allowed to warm up and acetic anhydride vapor was bled through the reaction vessel to a trap immersed in liquid nitrogen and a large gas reservoir connected to a Toepler pump. The undecomposed anhydride was caught in the cold trap along with any condensable products. The uncondensed gases filled the bulb and were periodically pumped off and stored over mercury for subsequent analysis. After a run the cold trap was warmed to room temperature and then immersed in dry ice. The remaining gases were pumped off and mixed with the uncondensed gases. For analysis the gases were passed through potassium hydroxide solution to remove carbon dioxide, bromine water for unsaturates and acid cuprous chloride for carbon monoxide. Hydrogen was estimated by combustion over copper oxide at 300°C and hydrocarbons by catalytic combustion in oxygen at 500°C.

In the static runs the lamp was warmed up and then shut off for the few seconds necessary to introduce the acetic anhydride vapor to the desired pressure and again turned on to start the reaction. Pressure changes were observed at periodic intervals. At the conclusion of the run the gases were pumped out and analyzed as in the dynamic runs. For runs made in the absence of mercury vapor the reaction vessel was isolated from mercury through gold-leaf traps. It was observed that in all runs, both static and dynamic, a brown deposit formed on the quartz of the lamp. It was never observed on any other part of the reaction vessel. The deposit was removed by filling the reaction vessel with oxygen and turning on the lamp. This was done after each run, the system being thoroughly evacuated and flushed with acetic anhydride vapor before a subsequent experiment.

For the runs made using the higher light intensity of the second reaction vessel, the mercury manometer was replaced with one containing dibutyl phthalate. The effect of temperature was studied by experiments at 80, 120, 140, 220, and 300°C. The effect of carbon dioxide and of ethane as diluents was studied at 80°C. To estimate the quantum yield a series of runs using formic acid was made at 80, 120, and 140°C. Finally, the undecomposed acetic anhydride and liquid products, collected from several runs, was distilled in a microrectification flask<sup>4</sup> and the first milliliter subjected to two tests. A part of this liquid was treated with an ammoniacal hydroxylamine solution and nickel sulfate added. A red precipitate of nickel dimethyl glyoxime showed the presence of biacetyl. The remainder of the liquid was heated with a large amount of salicylic acid and a few drops of concentrated sulfuric acid. The dis-

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15-min runs			Initial pressure 50-60 mm Percentages		
Temp. °C	CO2	со	C <sub>2</sub> H <sub>6</sub>	CH₄	H2
40	28	37	30	0	2
80	29	36	31	0	4
120	30	35	30	1	4
140	28	36	30	1	5
224	25	41	28	0	6
300	22	44	18	6	10

tinctive odor of wintergreen suggested the presence of methyl alcohol or methyl acetate in the distillate.

#### RESULTS

Preliminary experiments using the first reaction vessel in both static and flow runs, unsensitized and mercury sensitized, showed analyses of products at variance with those mentioned earlier of Berthelot and Gaudechon most especially in the absence of methane at low temperature. The analysis of products appeared to be independent of the presence or absence of mercury vapor though the rate of decomposition was about fifty percent faster in the mercury sensitized runs. Reproducibility with this lamp was poor partly due to the weak intensity of the absorbable radiation and the second lamp, a stronger light source, was used in all the remaining work.

Table I contains the averages of analyses of gaseous products from runs at a series of temperatures. The average error of each value is between one and two percent. At low temperatures it is apparent that CO<sub>2</sub>, CO, and C<sub>2</sub>H<sub>6</sub> are the principal products. Considering the experimental difficulty of separation of the less volatile and more soluble carbon dioxide and ethane from undecomposed reactant it seemed possible that all three products were produced in equal amounts equivalent to the complete decomposition of a molecule of acetic anhydride. Analyses after five, ten, and fifteen minute runs at the lower temperatures showed reproducibility for the carbon dioxide and ethar with a tendency for the carbon monoxide to be higher the shorter the run again reflecting its higher volatility and lower solubility in acetic anhydride. At the highest temperature however the course of reaction is obviously different showing unmistakable amounts of hydrogen and methane accompanying the decrease in carbon dioxide and ethane and corresponding increase in carbon monoxide. A material balance on the gaseous products of runs up to 224°C, assuming all the oxygen is present therein, yields formulas very close to C<sub>4</sub>H<sub>6</sub>O<sub>3</sub> while at 300°C, the formula is  $C_{3.5}H_5O_3$  suggesting a loss of  $(CH_2)_n$ .

Rate measurements in the absence of mercury vapor were made by following the pressure change on the dibutyl phthalate manometer during static experiments. Assuming acetic anhydride yields three products, the pressure of undecomposed anhydride could be calculated and plots of the logarithms of the anhydride pres-

<sup>&</sup>lt;sup>4</sup> Gettler and Siegel, Arch. Pathology 19, 208 (1935).

TABLE II. Specific reaction rates and temperature.

Temp. °C	k (min <sup>-1</sup> )
80	0.22
120	0.23
140	0.22
224	0.26

sure as a function of time gave excellent straight lines indicating a first-order rate to about seventy percent completion of reaction. Beyond this point deviations from linearity were apparent. Specific reaction rates were calculated from the slopes of these plots. In Table II these rates are listed for several different temperatures.

The 300°C runs could not be treated in the same manner since the decomposition could no longer be considered to be a splitting into three fragments. It was apparent however from the rate of pressure change that the course of reaction was quite different and was not further investigated.

In order to check the first-order rate found during a run, the dependence of rate on initial pressure was

TABLE III. Specific reaction rates and pressure.

$P_0$ (mm)	$k (\min^{-1})$
12.9	0.35
14.2	0.32
33.4	0.25
57.5	0.22

studied at four different pressures, all at 80°C. The results are given in Table III. In view of the variation in rate observed with change in initial pressure the effects of carbon dioxide and ethane as diluents were investigated at three different initial pressures of acetic anhydride. The data are listed in Table IV. The percentage of diluent was not determined very accurately because of experimental difficulties. The rates given as k are those calculated from the slopes of the rate curves; k'is the calculated specific rate at the specified initial pressure of acetic anhydride in the absence of diluent. It is apparent that at low pressures of the anhydride both carbon dioxide and ethane increase the rate while at high pressures the diluent effect is negligible.

A series of runs was made on formic acid from 80° to 140°C in order to determine quantum yields. Formic

TABLE IV. Specific reaction rate and diluents.

Percentage diluent	<b>P</b> <sub>0</sub> (mm)	k (min <sup>-1</sup> )	k' (min-1)
0	57.5	0.22	0.22
40 CO <sub>2</sub>	50.8	0.22	0.22
60 CO <sub>2</sub>	55.4	0.22	0.22
55 CO <sub>2</sub>	20.9	0.37	0.29
70 CO <sub>2</sub>	20.0	0.34	0.29
55 C.H.	17.6	0.36	0.30
$70 C_2 H_6$	19.7	0.30	0.29

acid exists as both monomer and dimer in the vapor phase and decomposes by two different mechanisms to give either carbon monoxide and water or carbon dioxide and hydrogen. The photolysis is first order and has a quantum yield of one over a wide range of temperature and pressure independent of the molecular weight of the starting material.<sup>5</sup> On the assumption that one molecule of the acid gives two molecules of product on photolysis, the rate of pressure change was plotted as logarithms of the undecomposed formic acid against time and the slope taken as the specific rate. At 80°, 120°, and 140° a constant specific rate of 0.10 min<sup>-1</sup> was found, independent of the pressure. Neither acetic anhydride nor formic acid absorb radiation above 2000A. The spectrum of neither has been accurately determined but what evidence there is points to high absorption near 1849A. The output of the lamp used consists mostly of 2537A radiation and from five to fifteen percent of the total at 1849A. What decomposition occurs is consequently to be attributed to the 1849A radiation and it has therefore been assumed that this radiation is completely absorbed by both the formic acid and the acetic anhydride over the same range of pressure. At comparable pressures the ratio of the rates is therefore the ratio of quantum yields. A rough estimate of the quantum yield of acetic anhydride in the temperature range 80-140°C is thus two at the higher pressures studied, increasing somewhat as the pressure is decreased.

#### DISCUSSION

Since the absorption in the 1849A region by acetic anhydride is high,<sup>6</sup> since the intensity in this region afforded by the lamp is low and since the rate of decomposition of the anhydride does not increase with increasing pressure, it is assumed that the radiation emitted by the lamp at 1849A is completely absorbed. On absorption of a quantum equivalent to about 150 kcal per mole, an excited molecule will be formed which may either decompose or be deactivated. The simplest mechanism consistent with the major observations is represented by the following reactions, in which I is the absorbed intensity,

$$(CH_{3}CO)_{2}O + h\nu \rightarrow (CH_{3}CO)_{2}O^{\ddagger}$$
(1)

$$(CH_{3}CO)_{2}O^{\pm} + M \xrightarrow{\sim}_{k_{2}} (CH_{3}CO)_{2}O + M$$
(2)

$$(CH_3CO)_2O^{\ddagger} \xrightarrow{2} 2CH_3 + CO + CO_2 \qquad (3)$$

$$CH_3 + (CH_3CO)_2O \xrightarrow{k_5} C_2H_6 + CH_3 + CO + CO_2$$
 (4)

$$2CH_3 \rightarrow C_2H_6. \tag{5}$$

The usual steady-state treatment yields for the over-all decomposition,

$$-d[(CH_3CO)_2O]/dt = k_3[(CH_3CO)_2O^{\pm}] + k_4[CH_3][(CH_3CO)_2O],$$
  
<sup>5</sup> E. Gorin and H. S. Taylor, J. Am. Chem. Soc., 56, 2042 (1934).  
<sup>6</sup> Ley and Arends, Z. physik. Chem., 17B, 177 (1932).

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and assuming the rate of reaction 3 small in comparison with that of 4,

$$-d[(CH_{3}CO)_{2}O]/dt$$

$$=k_{4}(4k_{3}I/k_{5}(k_{2}[M]+k_{3}))^{3}[(CH_{3}CO)_{2}O]$$

$$=k[(CH_{3}CO)_{2}O],$$

if [M] is constant, in agreement with the first-order rate observed and the approximate equivalence of the amounts of CO, CO<sub>2</sub> and C<sub>2</sub>H<sub>6</sub>. This picture is probably much over-simplified, since CO is found to be consistently higher than CO<sub>2</sub> with C<sub>2</sub>H<sub>6</sub> intermediate but nearer that of CO<sub>2</sub> though the difference may be experimental. In addition the presence of biacetyl and methyl acetate has been demonstrated. Inspection of reactions (3) and (4) will show their improbability as single step reactions and the following seem reasonable alternative mechanistic steps:

 $CH_3 + (CH_3CO)_2O \xrightarrow{k_4'} C_2H_6$ 

 $+CH_3COOCO \rightarrow CH_3CO + CO_2$  (4')

$$2CH_{3}CO \rightarrow (CH_{3}CO)_{2}$$
(6)

$$2CH_3COO \rightarrow C_2H_6 + 2CO_2 \tag{7}$$

$$CH_3 + CH_3COO \rightarrow CH_3COOCH_3$$
 (8)

$$CH_3CO \rightarrow CH_3 + CO.$$
 (9)

In reaction (3') the excited anhydride molecule has absorbed 150 kcal per mole. If 80 kcal are used in breaking C-C bonds, 70 kcal remain and the methyl radicals would be expected to take about 60 of these. Such methyl radicals would be expected to yield methane in quantity whereas no methane is observed. The radical CH<sub>3</sub>COOCO must thus be electronically excited and could decompose in either of two ways. If it splits out CO<sub>2</sub>, the energetic acetyl radical remaining would most probably break down into a methyl radical and CO<sub>2</sub> a reaction requiring 18 kcal energy of activation.<sup>7</sup> This sequence of reactions is equivalent to reaction (3).

An alternative possibility for the electronically excited CH<sub>3</sub>COOCO radical would be to split out carbon monoxide producing an acetate radical. Judging from acetic acid photolysis the acetate radical is fairly stable and it has been estimated that 40 to 70 kcal are required to decompose it.<sup>8</sup> Reaction (7) is a step postulated in acetic acid photolysis and reaction (8) with a higher probability in the presence of methyl radicals accounts for the methyl acetate found.

<sup>7</sup> D. S. Herr and W. A. Noyes, J. Am. Chem. Soc. **62**, 2052 (1940). <sup>8</sup> M. Burton, J. Am. Chem. Soc., **58**, 1655 (1936). Reaction (4) similarly may be analyzed in terms of steps (4') and (9), the CH<sub>3</sub>COOCO radical not now being excited can probably only split out carbon dioxide, the residual acetyl radical not necessarily decomposing but being a potential source of the biacetyl observed.

From 80° to 224°C the specific reaction rate is constant suggesting that none of the major steps in the reaction has an appreciable activation energy. Since the excited acetic anhydride molecules have absorbed 150 kcal per mole, the fragments of the decomposition are energetic enough to break down without additional thermal activation. At 300°C the decomposition rate appears faster, methane is present in considerable amount and ten percent of the gaseous products are hydrogen. It is apparent that the mechanism is changed due no doubt to the possibility of thermal activation.

The rate of photolysis of acetic anhydride at 80°C increases as the initial pressure, a, decreases. The change is expressible by the empirical relation:  $k_{obs} \cdot \log a = 0.38$  $\pm 0.01$ . While no reason can be adduced for the logarithmic relation, an attempt can be made to explain the fact of a pressure dependence of the rate as well as the effect of added diluent. Comparison of the photolysis of acetic anhydride with that of formic acid under the assumptions previously noted shows that the quantum yield lies around 2-4, the highest value for the lowest initial pressure. The kinetic analysis shows reaction (4) more nearly rate-controlling and more important than (3). Reaction (2), the deactivation of excited acetic anhydride molecules must therefore be considerable to balance the chains of reaction (4). In addition since the reaction is first order, [M] must be constant for a given run. As a deactivating molecule, acetic anhydride by its many modes of vibration should be very efficient, the most efficient of all molecules present. The product molecules ethane, carbon dioxide, and carbon monoxide having each approximately onethird the mass of acetic anhydride and correspondingly fewer vibrations would be less efficient as deactivating agents. If it is assumed tentatively that each is onethird as efficient, since per molecule decomposed approximately these three are produced, deactivation will remain constant throughout a run.

At high initial pressures of acetic anhydride, deactivation will be very efficient and further increase of pressure will have little effect on the rate. Had it been possible to carry the study to higher pressures than those used a rate constant independent of pressure might have been demonstrated. The low vapor pressure of the anhydride precluded this possibility in the apparatus used.

At low pressures of the anhydride the rate has been shown to increase. The concentration of excited molecules is given by the expression  $I/(k_2[M]+k_3)$  and with the above assumptions [M] may be replaced approximately by, a, the initial pressure. From this  $k_{obs} = k_4 (4k_3 I/k_5 (k_2 a + k_3)^{\frac{1}{2}}$  and is shown experimentally to be given by  $0.38/\log a$ , the rate increasing as the pressure is decreased. With added diluent, however, [M] can no longer be replaced by a, but for example with carbon dioxide as diluent, [M] becomes approximately  $a + [CO_2]/3$ . When a is large the effect of the added term on  $k_{obs}$  will be small but will become more effective the lower the initial pressure; collisions between excited anhydride molecules and diluent being only approximately one-third as effective cause an increase in rate. This is observed, in fact, the rate observed with a starting mixture of approximately three parts of ethane to one part of acetic anhydride is almost identical with the rate in the absence of diluent. Carbon dioxide, which would not be expected to be as efficient

for deactivating as ethane, shows a higher rate than that in the absence of diluent.

The suggested mechanism accounts at least qualitatively for the experimental observations. The suggested steps have all been postulated previously in other studies. Many additional steps could conceivably be written and have been considered and rejected as incompatible either with the observed order of the rate or with the product analysis. Several consequences of the postulated mechanism are under further investigation and will be reported later. The possibility of a mercury sensitized reaction has not been overlooked as accounting particularly for the diluent effect observed. It is believed, however, that the precautions taken rendered the system free from mercury.

THE JOURNAL OF CHEMICAL PHYSICS VOLUME 19, NUMBER 10 OCTOBER, 1951

## The Ionization Potentials of the Deuterated Methanes\*

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The ionization potentials of methane, and of the four deuterated methanes, have been determined by electron impact using two 90° mass spectrometers with different types of sources. In addition, the ionization potentials of acetylene, deuterated acetylene, ethylene, and deuterated ethylene have been measured. A simple empirical method is used to obtain values which are reproducible to  $\pm 0.02$  volt. For the methanes the ionization potential is found to increase with the number of deuterium atoms in the molecule, with a difference of 0.18 volt between the value for  $CH_4$  and that for  $CD_4$ . Although this difference is found to be the same on each of the mass spectrometers, there is a difference of 0.11 volt between the absolute values of the ionization potential as determined for CH4 on the two instruments. In order to explain the difference between the ionization potentials of CH<sub>4</sub> and CD<sub>4</sub> on the basis of zero point energy differences, it is estimated that the force constants in the ionic state would need to have only about 1 of their value in the ground state. Since this seems unreasonably low, it is suggested that the difference between the ionization potentials of the methanes, as measured by electron impact, may be caused, in part, by excess energy required for a "vertical" transition.

#### INTRODUCTION

URING the last few years deuterated compounds have been used often in kinetic studies. As a result, the analysis of the deuterated products, usually hydrocarbons, by means of a mass spectrometer has become important. A property of great interest in analyzing mixtures of deuterated hydrocarbons is the ionization potential.<sup>1</sup> Spectroscopic values are available for only a few simple molecules and, although considerable work has been done on the determination of ionization potentials by electron impact,<sup>2-5</sup> no data

<sup>3</sup> R. E. Honig, J. Chem. Phys. 16, 105 (1948).
<sup>3</sup> M. B. Koffel and R. A. Lad, J. Chem. Phys. 16, 420 (1948).
<sup>4</sup> J. J. Mitchell and F. F. Coleman, J. Chem. Phys. 17, 44 (1949).
<sup>5</sup> D. P. Stevenson and J. A. Hipple, J. Am. Chem. Soc. 64, 1588, 2766, 2769 (1942); 65, 209 (1943).

have been reported on the ionization potentials of a complete deuterium-substituted series. Honig<sup>2</sup> has reported values of 13.04 volts for  $CH_4$  and 13.21 volts for  $CD_4$ . In this work the ionization potentials of the five hydrogen-deuterium isomers of methane have been determined by an electron impact method.

Various methods of obtaining the ionization potential from ionization efficiency curves have been employed. The extrapolation of the straight line portion of the curve, although used with some success by Vought<sup>6</sup> and by Koffel and Lad<sup>3</sup> seems in general to be the least preferred of the methods available. Stevenson and Hipple<sup>5</sup> have obtained consistent results by measuring the point of initial onset. More recently Honig,<sup>2</sup> and Mitchell and Coleman,<sup>4</sup> have used methods based on the shape of the initial portion of the curve. For comparing the ionization potentials of molecules as similar as those of the deuterated methanes, any of these methods would probably be satisfactory. The accurate determination of absolute values of the ionization

<sup>6</sup> R. H. Vought, Phys. Rev. 71, 93 (1947).

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<sup>&</sup>lt;sup>1</sup>D. P. Stevenson and C. D. Wagner, J. Am. Chem. Soc. 72, 5612 (1950).