

Photochemical Studies by Means of a Field Ion Mass Spectrometer

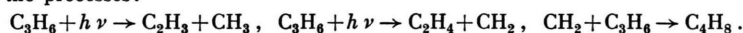
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A mass spectrometric investigation was carried out on the direct photolyses of propene, 1-butene, and hydrazine at 1849 Å with a field ion source in a flow system. Comparisons were made with Pt tip and wire emitters. It was found that, without illumination, mass spectra obtained with the wire were accompanied by a number of fragment peaks amounting to almost 1%. Since these peaks interfere with those produced photochemically, the tip emitter was used mostly for the photochemical studies although it gave 100 times less current and was less stable. The photochemical products formed at a gas pressure of 10 μ by a low pressure mercury lamp were detected after approximately 10 m sec. The three main peaks observed in the propene photolysis were at masses 27, 28, and 56, indicating the processes:



The photolysis of 1-butene gave four main peaks at masses 40, 41, 42, and 70, suggesting steps, $\text{C}_4\text{H}_8 + h\nu \rightarrow \text{C}_3\text{H}_4 + (\text{H} + \text{CH}_3)$ or CH_4 , $\text{C}_4\text{H}_8 + h\nu \rightarrow \text{C}_3\text{H}_5 + \text{CH}_3$, $\text{C}_4\text{H}_8 + h\nu \rightarrow \text{C}_3\text{H}_6 + \text{CH}_2$, $\text{CH}_2 + \text{C}_4\text{H}_8 \rightarrow \text{C}_5\text{H}_{10}$.

The only peak found with the photolysis of hydrazine was at mass 17, indicating the step,



The possibility of forming these products by secondary processes is discussed.

The direct detection of radicals formed in unsensitized primary photochemical processes is almost impossible by conventional mass spectrometry since the concentration of radicals produced is extremely small. In order to produce a large concentration of radicals, KISTIAKOWSKY and KYDD¹ used the flash photolysis technique in conjunction with a time-of-flight mass spectrometer. LOSSING and his coworkers² took advantage of mercury (³P₁) sensitization. Since the absorption coefficient of mercury vapor at 2537 Å was extremely large, it was possible to produce large concentrations of radicals which could be detected by a conventional electron-impact mass spectrometer. The photodissociation of amines was studied mass spectrometrically by TERENCE and his coworkers³. In order to avoid fragmentation of the molecule by electron impact, low energy electrons were used for ionization.

The main difficulty encountered in photolysis studies by conventional mass spectrometry is that extensive fragmentation of parent ions takes place

with electron impact. In many cases, fragment ions produced in this way have the same masses as those produced photochemically. Thus, it is necessary to produce large concentrations of radicals (more than 10%) to make reliable measurements. This can be overcome by using a field ion source instead of an electron impact source.

It was first discovered by GOMER and INGRAM⁴ that ions formed with high electric field (~10⁸ V/cm) display very little fragmentation. Field ionization became, therefore, suitable for the study of photochemical processes. The work was further extended⁵ to include hydrocarbons and amines. BECKEY and GROTH⁶ made the first application of this method to study the photolysis of acetone at 2537 Å. Since the fragment peak (CH_3CO^+) was so small (3.5×10^{-4} of the parent peak), it was possible to detect 1.4×10^{-3} of CH_3CO produced photochemically.

The purpose of this work is to study mass spectrometrically the direct photolysis of some gases

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¹ G. B. KISTIAKOWSKY and P. H. KYDD, J. Amer. Chem. Soc. 79, 4825 [1957].

² F. P. LOSSING, Mass Spectrometry, McGraw-Hill Book Company, Inc., New York 1963, p. 442.

³ F. I. VILESOV, B. L. KURBATOV, and A. N. TERENCE, Dokl. Akad. Nauk SSSR 122, 94 [1958].

⁴ R. GOMER and M. G. INGRAM, J. Amer. Chem. Soc. 77, 500 [1955].

⁵ H. D. BECKEY, Bull. Soc. Chim. Belges 73, 326 [1964].

⁶ H. D. BECKEY and W. GROTH, Z. Phys. Chem. NF 20, 307 [1959].



at 1849 Å with a field ion source. Three gases, propene, l-butene, and hydrazine, were chosen since they (a) have high absorption coefficients at 1849 Å, (b) have very little field dissociation, and (c) give relatively large emission current.

Experimental

The field ion source, attached to the Atlas CH-4 mass spectrometer, was similar in design to that described previously⁷. As is shown in Fig. 1, it

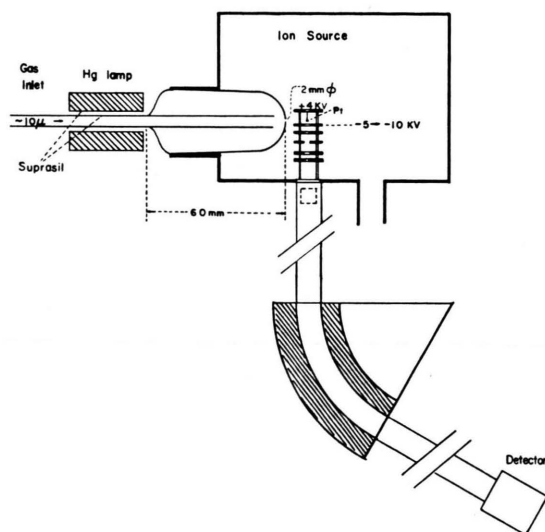


Fig. 1. Arrangement for photochemical studies by a field ion mass spectrometer.

was modified to accommodate the reaction chamber provided with a hole of about 2 mm diameter at the end through which the gas flowed into the ion source. The reaction chamber, a Suprasil tube of 8 mm i. d., was situated approximately 60 mm from the hole. The lamp was a Lossing type⁸ low pressure mercury lamp with the exception that the inner wall was made of Suprasil to transmit light of wavelength at 1849 Å. The lamp intensity at this wavelength was approximately 10^{17} quanta/sec in the 2 cc reaction volume⁹.

The pressure of the flowing gas was maintained at about 10μ which was read on a Leybold thermotron pressure gauge. The residence time of

the gas in the illuminated zone was estimated from the leak rate to be approximately 10 msec. The method of preparation of the Pt tip¹⁰ and wire¹¹ has been previously described. The anode was maintained at +4 kV. A cathode potential of -9 kV was applied to the tip and -5 kV for the wire. Matheson C. P.-grade propene and l-butene were used without further purification. Hydrazine, obtained from Fluka A. G., was fractionally distilled in a He atmosphere.

Results and Discussion

A. Comparison of the Mass Spectra with Wire and Tip Emitters

The advantage of using wire instead of tip emitters has already been described¹¹. The fluctuation of the ion intensity decreases considerably by the use of the wire due to the increase of emission surface. It was thought that wire would be better suited for photochemical studies.

Typical total emission current for the wire was about 10^{-8} A and, for the tip, about 10^{-10} A. The mass spectra were taken with Pt wire and Pt tip emitters for comparison purposes. Fig. 2 shows the spectra of acetone. It is apparent that the spectrum with the wire emitter contains many peaks other than that at mass 43. The origin of these peaks is not entirely clear. The parent-plus-one peak is larger in the case of the wire, amounting to 40% of the parent peak, suggesting a larger extent of ion-molecule reactions on the surface¹².

The spectra of l-butene are shown in Fig. 3. The spectrum with the wire contains many fragment peaks which are entirely absent with the tip emitter. The parent-plus-one peak is also larger with the wire emitter. The spectrum of hydrazine with the wire showed a peak at mass 17 which was absent when the tip was used. Furthermore, it was observed that the parent-plus-one was the main peak with the tip. Fragment peaks with the wire amount to, at most, 1% of the parent peak in all cases. These fragment peaks do not present serious problems for analysis of mixtures of stable molecules. However, the occurrence of these peaks seriously limits the

⁷ H. D. BECKEY, Z. Naturforschg. **17** a, 1103 [1962].

⁸ F. P. LOSSING, D. G. H. MARSDEN, and J. B. FARMER, Canad. J. Chem. **34**, 701 [1956].

⁹ H. D. BECKEY, W. GROTH, H. OKABE, and H. J. ROMMEL, Z. Naturforschg. **19** a, 1511 [1964].

¹⁰ H. D. BECKEY and G. WAGNER, Z. Anal. Chem. **197**, 58 [1963].

¹¹ H. D. BECKEY, Z. Anal. Chem. **197**, 80 [1963].

¹² H. D. BECKEY, Z. Naturforschg. **15** a, 822 [1960].

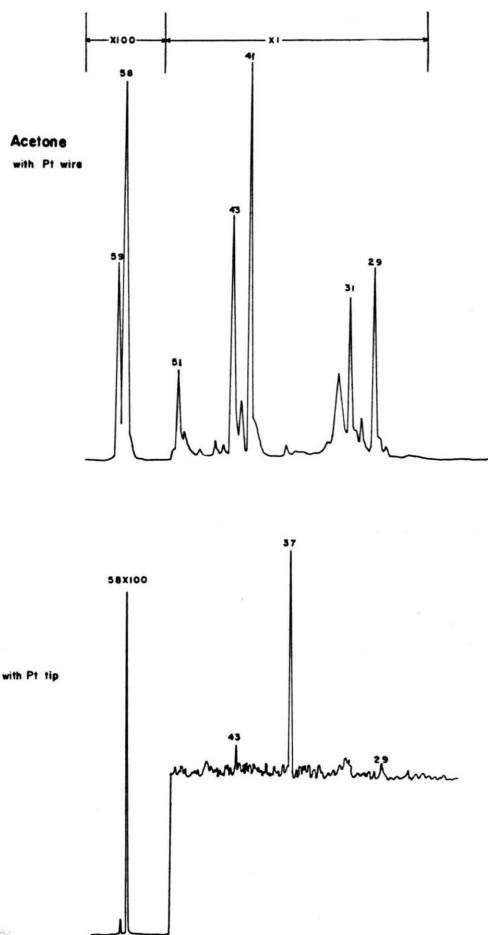


Fig. 2. Field ion mass spectra of acetone with Pt wire and tip.

accuracy of the detection of radicals produced photochemically. Therefore, it is much more desirable to use tips for photochemical studies where radical concentrations are extremely small. The fluctuation of ion current is large, however, amounting to almost $\pm 30\%$ with the tip. The subsequent experiments were performed mostly with the Pt tip emitter.

B. Photochemical Reactions at 1849 Å

The gases propene, l-butene, and hydrazine, were studied. The absorption coefficients (base e) are $300 \text{ atm}^{-1} \text{ cm}^{-1}$ ¹³, $500 \text{ atm}^{-1} \text{ cm}^{-1}$ ¹³, and $800 \text{ atm}^{-1} \text{ cm}^{-1}$ ¹⁴, respectively, at 1849 Å. The absorption at 2537 Å is negligibly small. The field

¹³ J. A. R. SAMSON, F. F. MARMO, and K. WATANABE, *J. Chem. Phys.* **36**, 783 [1962].

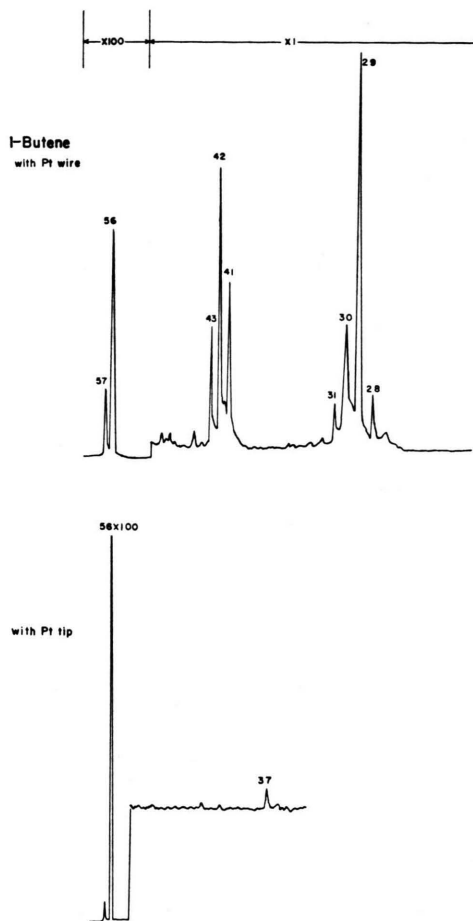


Fig. 3. Field ion mass spectra of l-butene with Pt wire and tip.

dissociation of propene and l-butene with the tip is extremely small¹⁵.

Typical ion current at the main peak was about 10^{-13} A at the electron multiplier. In each case, it was demonstrated that the photochemical reaction took place only with light of wavelength at 1849 Å since no new peak appeared during illumination with a Vycor filter to cut off light at 1849 Å.

From the leak rate through the hole of 2 mm diameter, it can be estimated that radicals formed at the illuminated zone are detected after approximately 10 msec. During this time a radical suffers approximately 10^3 collisions at 10μ pressure. Since the concentration of radicals is about 0.1%, the radical-radical interaction may be neglected. This

¹⁴ C. C. McDONALD, A. KAHN, and H. E. GUNNING, *J. Chem. Phys.* **22**, 908 [1954].

¹⁵ P. SCHULZE, Dissertation, The University of Bonn, 1964.

is substantiated by the observation that no peak of recombination product of C_2H_3 or C_3H_5 was found. However, any radical-reactant interaction is expected to occur if the collision yield is more than 10^{-3} .

1. Photolysis of Propene

The spectra of propene with and without illumination are shown in Fig. 4. New peaks are observed with illumination at masses 27, 28, and 56. The intensity ratio, M_{27}/M_{28} , was almost independent of

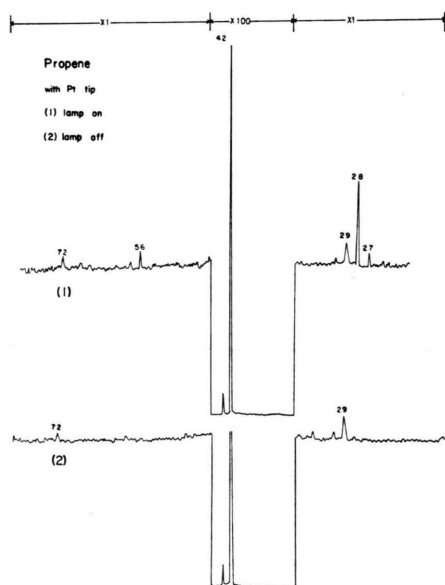
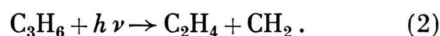
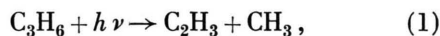


Fig. 4. Field ion mass spectra of propene with Pt tip (1) during illumination at 1849 Å and (2) without illumination.

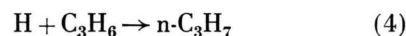
pressure over the range from 1 to 10μ whereas the intensity at mass 56 increased with pressure. Because of the presence of fragment peaks at masses 40 and 41, amounting to almost 0.3% of the parent peak without illumination, it was difficult to ascertain whether they increased with illumination. The peaks at masses 27 and 28 indicate primary processes



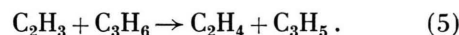
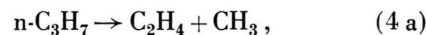
The most likely secondary process forming butenes at mass 56 is



Other probable secondary processes are,

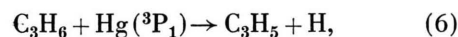


followed by,



The collision yield of Step (4) was shown to be 10^{-5} ¹⁶. Since the ratio M_{27}/M_{28} is almost independent of the pressure, Reaction (5) does not appear to be important. No information is available for the rate of Reaction (5). The relative butene peak intensity increases with pressure which is indicative of Reaction (3). It is not clear whether allene or allyl is formed photochemically because of the experimental difficulties mentioned before. Radicals CH_2 and CH_3 were not detected either because of their low field ionization efficiency⁶ or of their reaction with propene. Acetylene, a major product in the photolysis at 1849 Å¹⁷, was not found probably because of its higher ionization potential than that of ethylene. At 1236 Å and 1470 Å, more primary processes appear to be involved besides Steps (1) and (2)¹⁸.

In contrast with the photolysis at 1849 Å, major primary processes in the $Hg(^3P_1)$ sensitized reaction are¹⁹,

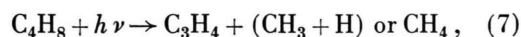


No molecular detachment process was observed.

2. Photolysis of 1-Butene

The result of the photolysis of 1-butene is shown in Fig. 5. New peaks were observed at masses 40, 41, 42, and 70 during illumination. Small peaks were detected at masses 15 and 27. The pressure was kept constant at 10μ during the experiments. Because of the background peaks at masses 54 and 55, amounting to 0.2%, it was not possible to measure, with certainty, the change of these peaks with the lamp on. With the wire emitter, only one peak at mass 40 was found.

Corresponding to the new peaks at masses 40, 41, and 42, three probable primary processes are,



¹⁶ C. A. HELLER and A. S. GORDON, J. Chem. Phys. **42**, 1262 [1965].

¹⁷ S. ARAI, T. NISHIKAWA, and S. SHIDA, private communication.

¹⁸ D. A. BECKER, H. OKABE, and J. R. McNESBY, J. Phys. Chem. **69**, 538 [1965].

¹⁹ M. AVRAHAM and P. KEBARLE, J. Phys. Chem. **67**, 354 [1963].

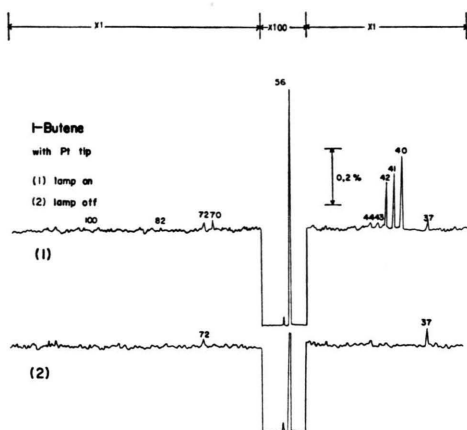
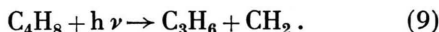
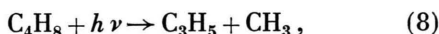


Fig. 5. Field ion mass spectra of 1-butene with Pt tip (1) during illumination at 1849 Å and (2) without illumination.



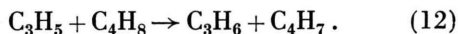
Pentenes are probably formed from



Other possible secondary reactions are



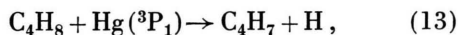
followed by



The collision yield of Reaction (11) is approximately 10^{-2} ²⁰. It is likely that Reaction (11a) might contribute to the formation of propene. The rate of Reaction (12) does not appear to have been measured. No further study was made at various pressures to confirm Reaction (12).

The preferential C—C bond split ($\text{C}_3\text{H}_5-\text{CH}_3$) can be explained on the basis of the bond energy difference $D(\text{C}_2\text{H}_3-\text{C}_2\text{H}_5) - D(\text{C}_3\text{H}_5-\text{CH}_3)$ of 28 kcal/mole²¹. From the product analysis in the high pressure region (1–125 torr) at 1849 Å, it was concluded also that Reaction (8) [$\text{C}_3\text{H}_5-\text{CH}_3$ bond split] and Reaction (9) [propene elimination process] are important primary processes²². On the other hand, two primary steps are important

in the $\text{Hg}(^3\text{P}_1)$ sensitized reaction⁸.



No molecular detachment processes of the types (7) and (9) were observed.

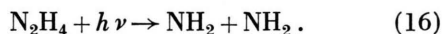
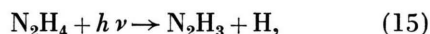
Nearly 1% of the light is absorbed at 10μ with 1 cm path length and an absorption coefficient of 500 cm^{-1} . Since the intensity of the lamp at 1849 Å is 10^{17} quanta/sec in 2 cc reaction volume⁹, 10^{13} quanta of light are absorbed in 10 msec. Since there are approximately 8×10^{14} molecules in the reaction volume and there are more than three primary processes, each peak height must be less than 0.3% of the parent assuming the same sensitivities of products as that of the reactant. Experimentally, approximately 0.2% of the peak height was found for each process.

3. Photolysis of Hydrazine

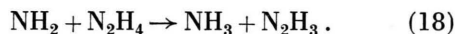
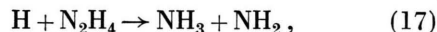
Figure 6 shows the spectra of hydrazine with the lamp on and off. The only new peak observed was that at mass 17. The spectrum was similar either at 10μ or at 20μ . The peak at mass 17 indicates the process



The earlier experiments^{23, 24} indicate the occurrence of two primary reactions,



No peak was observed either at mass 15 or 16. It is possible that NH_2 is not detected because of its relatively high ionization potential of 11.3 eV²⁵. The ionization potential of NH does not seem to have been measured. The possible secondary reactions to produce NH_3 are:



No information on rates of these reactions is available.

²⁰ K. R. JENNINGS and R. J. CVETANOVIC, *J. Chem. Phys.* **35**, 1233 [1961].

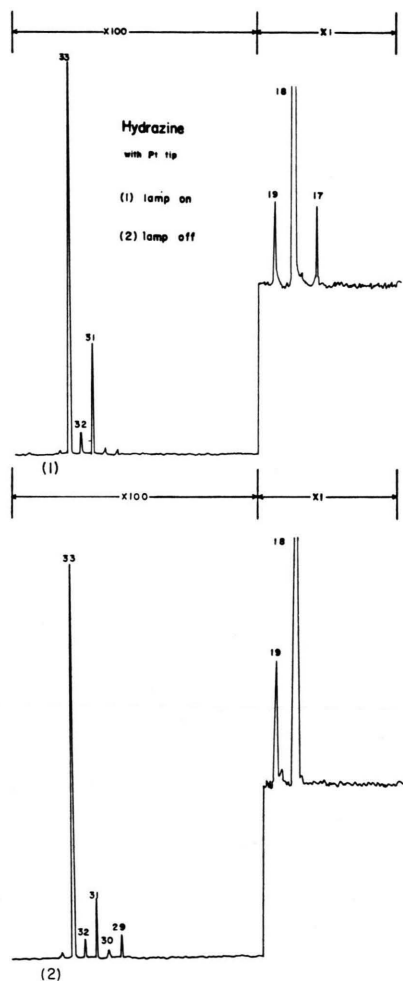
²¹ Calculated from the table by A. F. TROTMAN-DICKENSON, *Gas Kinetics*, Academic Press, Inc., New York 1955, p. 15.

²² N. HARUMIYA, S. SHIDA, and S. ARAI, *Bull. Chem. Soc. Japan* **38**, 142 [1965].

²³ C. H. BAMFORD, *Trans. Faraday Soc.* **35**, 568 [1939].

²⁴ D. A. RAMSAY, *J. Phys. Chem.* **57**, 415 [1953].

²⁵ M. M. MANN, A. HUSTRULID, and J. T. TATE, *Phys. Rev.* **58**, 340 [1940].



Conclusion

It has been shown that a field ion mass spectrometer could be applied successfully to study certain photochemical reactions which would otherwise be difficult to study. This work is of qualitative nature and further work is needed to obtain more quantitative results. It is not as yet well established whether certain products originate from primary or secondary processes. More work on the effect of pressure and isotopic studies should help to answer this question.

Acknowledgements

We are indebted to the Deutsche Forschungsgemeinschaft for financial support of this work. One of us (H. O.) thanks the Deutsche Forschungsgemeinschaft for a fellowship.

Fig. 6. Field ion mass spectra of hydrazine with Pt tip (1) during illumination at 1849 Å and (2) without illumination.