

[CONTRIBUTION FROM THE EVANS CHEMICAL LABORATORY, THE OHIO STATE UNIVERSITY, COLUMBUS 10, OHIO]

Detection and Lifetime of Enol-Acetone in the Photolysis of 2-Pentanone VaporBY G. R. McMILLAN,¹ JACK G. CALVERT, AND JAMES N. PITTS, JR.

RECEIVED MARCH 16, 1964

The formation of the *enol* form of acetone in the "type II" primary photochemical process in methyl ketones containing γ -hydrogen atoms has received general acceptance in recent years on the basis of published indirect evidence. In this work a direct observation of the transient *enol* form of acetone has been made by infrared absorption during the photolysis of 2-pentanone. The *enol* \rightarrow *keto* conversion was studied by following both the disappearance of the *enol* and the appearance of the *keto* form using long-path infrared techniques. The half-life of *enol*-acetone is about 3.3 min. at 27° and 750-mm. total pressure. The ketonization process seems to occur mainly at the reaction vessel wall. Photolyses of 2-pentanone were also carried out in small reaction vessels pretreated with D₂O. In this case the *keto*-acetone ultimately produced is partly monodeuterated, and a partial exchange of the *enol* form at the vessel wall is indicated; this result is similar to that reported by Srinivasan in experiments with 2-hexanone. The extent of exchange exhibits a peculiar dependence on the residence time in the cell which complicates the interpretation of the ketonization step under these conditions.

Extensive work on the photochemistry of ketones containing γ -hydrogen atoms has revealed participation of several primary processes. Most attention has been claimed by the "type II" process in which an olefin and a methyl ketone are eventually formed.² In a study of the 2-hexanone photolysis, Davis and Noyes³ suggested a transfer of a γ -hydrogen directly to the carbonyl oxygen, with decomposition to give propylene and the *enolic* form of acetone. The formation of such a transient *enol*, which might possess a readily exchangeable hydrogen, was later invoked⁴ to explain some unexpected results on the deuterium content of acetone formed in photolysis of 2-pentanone-1,1,1,3,3-*d*₅.⁵ The formation of the *enol* in the primary process in these ketones has been widely accepted since the appearance of Srinivasan's report⁶ that acetone produced in 2-hexanone photolysis could exchange one hydrogen at the vessel surface.

In the present study of vapor phase photolysis of 2-pentanone, we have attempted to detect the transient *enol*-acetone in infrared absorption in a long-path spectrometer, to measure its lifetime, and to study the reactions leading to the *keto* form of the product always found by the conventional analysis.

Experimental

Materials.—The 2-pentanone used in most experiments, Bios Chemical Co. pentanone, was fractionally distilled. All samples were free of 3-pentanone, but some samples contained small varying amounts (<0.5%) of an unidentified impurity found by gas chromatography. The 1-methylcyclobutanol (b.p. 118° (742 mm.)) was prepared according to the method of Semenov, Cox, and Roberts.⁷ We were unable to isolate a pure sample of the compound from the products of photolysis of 2-pentanone in cyclohexane solution.⁸ Although this product was present in the solution after several days of exposure, it could not be separated cleanly from the complex reaction mixture which resulted from this procedure.

Experiments Using the Large Reaction Cell.—The large cell was a 60-l. cylindrical aluminum tank, radius 14 cm., enclosing the mirror support beam of the long-path attachment to the Perkin-Elmer Model 21 infrared spectrophotometer. The tank was fixed to the spectrometer housing through an O-ring seal. The two sodium chloride windows for the infrared beam and the six quartz windows for the admission of ultraviolet light were

sealed into place with Glyptal. Air leak rates as low as 1 μ /hr. have been obtained using this arrangement; with normal usage the rate of pressure rise due to degassing of the interior surfaces is somewhat greater.

The character of the vessel wall was changed over the course of this study. The aluminum paint surface⁹ used in some early experiments was covered with a layer of shiny aluminum foil. In other experiments a 50% coverage of the wall with small soft glass plates was obtained by taping the plates to the inner surface. The transport time for gas molecules to reach the wall was estimated using ozone; in these experiments a highly reactive wall was prepared by deposition of soot on the aluminum surface using a candle flame. In some experiments the surface was changed by treatment with D₂O vapor.

The quartz windows admitted light from three Hanovia Type A, 550-w. medium pressure mercury arcs held in a quartz water-cooled condenser. The radiation absorbed by the ketone was in the range 2300–3200 Å. in most of the experiments. Corning 9863 filters were interposed between the lamps and the windows in one series of experiments to remove wave lengths <2400 Å. and >4000 Å. In an earlier publication¹⁰ it was pointed out that admission of high intensity ultraviolet light to the cell created a spurious signal in the spectrometer. Since this occurs even when the cell is evacuated, it is presumed to be due to sudden heating and slight warping of the mirror support beam. In any case, covering the beam with mica or glass sheets and aluminum foil reduced the spurious pen displacement. Careful realignment of the infrared optical system and prevention of direct illumination of the mirrors also minimized the problem. Under the conditions used in this work the effect was negligible.

Most experiments were carried out at a reaction temperature of 27°. For one series the entire room was cooled to bring the cell temperature to 15°.

During an experiment, the infrared transmittances of compounds of interest were followed at 26-in. path length using the X5-scale expansion capability of the instrument. The wave length was locked at an appropriate value and the recorder thus drew the transmittance as a function of time.

Following some experiments, the cell contents were trapped using the multiple loop method already described.¹⁰ The method was quantitative even for ethylene at cell pressures of 0.1 mm. The 1-methylcyclobutanol was separated by gas chromatography on Carbowax at 75° and was analyzed by infrared absorption. Recovery from the chromatograph was only about 25% efficient for this compound; because of the large correction, the amount of alcohol reported for these runs is very approximate.

Exchange Experiments Using the Small Cells.—Two small cells were used for the photolysis of 2-pentanone at 27°; one was constructed of quartz, the other of soft glass but fitted with a quartz window waxed into place. Both vessels were 3 cm. in diameter and 15 cm. in length. Before each experiment the cell was treated with D₂O vapor at a pressure of 17 mm., then isolated and allowed to stand for 5 min. After this period, the water vapor was pumped away over a 5-min. period. The schedule was repeated except that successive samples of D₂O vapor were allowed to stand in the cell for 8, 11, and 15 min.

(1) Department of Chemistry, Western Reserve University, Cleveland 6, Ohio.

(2) C. H. Bainford and R. G. W. Norrish, *J. Chem. Soc.*, 1504 (1935).

(3) W. Davis, Jr., and W. A. Noyes, Jr., *J. Am. Chem. Soc.*, **69**, 2153 (1947).

(4) J. T. Graver and J. G. Calvert, *ibid.*, **80**, 3524 (1958).

(5) J. R. McNesby and A. S. Gordon, *ibid.*, **80**, 201 (1958).

(6) R. Srinivasan, *ibid.*, **81**, 5061 (1959).

(7) D. A. Semenov, E. F. Cox, and J. D. Roberts, *ibid.*, **78**, 3221 (1956).

(8) N. C. Yang and D. D. H. Yang, *ibid.*, **80**, 2913 (1958).

(9) N. R. Subbaratnam and J. G. Calvert, *ibid.*, **84**, 1113 (1962).

(10) G. R. McMillan, J. G. Calvert, and S. S. Thomas, *J. Phys. Chem.*, **68**, 116 (1964).

After a final evacuation period of 10 min., sufficient ketone was condensed into the cell to give a pressure of 12.2 mm. at room temperature. The choice of conditions was made in an attempt to reproduce those employed by Srinivasan⁶ in his study of 2-hexanone.

The light source for this series was a d.c. operated, PEK 200-w. high pressure mercury arc of output such that the radiation absorbed by the ketone was limited to the range 2900–3200 Å. The light intensity was varied using neutral density filters. Conversion was maintained at about 15% in most experiments.

After the illumination, the product acetone was separated by either gas chromatography on Carbowax at 75° or by fractional distillation and analyzed with the mass spectrometer. The 1-methylcyclobutanol in these experiments was identified and analyzed by gas chromatography but not by product isolation. The cell contents from experiments with normal pretreatment contained traces of water, as shown by gas chromatography.

Results

Observations of the Enol-Acetone.—Vapor of 2-pentanone at a pressure of 1.6 mm. was illuminated with the unfiltered light of the mercury arcs in the presence of 750 mm. of nitrogen, and the infrared absorption of the mixture was examined in the wave length region 2.5–3.0 μ . A small peak, amounting to about 4% deflection on X5-scale expansion, was found at 2.756 μ .¹¹ The peak disappeared in a few minutes after light was excluded from the cell. The instrument was locked on wave length 2.756 μ and the recorder drum was turned so that the pen drew the transmittance along a time abscissa. When the light was admitted to the cell, the transmittance decreased for about 5 min. and then reached a nearly constant value. When the light was suddenly excluded, the transmittance slowly increased to a constant value slightly lower than the transmittance before illumination. The half-life of the absorbing species measured in this way showed no variation with time of illumination over a range of 4–14 min. In the vessel lined with aluminum foil, the average half-life of 17 determinations was 3.34 ± 0.11 min. (standard deviation). In the vessel partly lined with glass, the average half-life was 4.7 ± 0.3 min., but in this case only three determinations were made. After extended illumination, a small nontransient peak was found at about 2.73 μ , probably due to 1-methylcyclobutanol.

The Delayed Formation of Keto-Acetone.—Formation of the *keto* form of acetone was studied by examining the infrared absorption at 8.15 μ . Admission of ultraviolet light to the cell caused a slow decrease in transmittance. After exclusion of light the transmittance continued to decrease for some minutes. The half-times for *keto*-acetone formation following cessation of illumination are given in Table I for different conditions.

Along with acetone, ethylene is produced in the type II primary process in 2-pentanone. Determination of the half-time for ethylene formation (absorption at 10.5 μ) gave a value of about 0.3 min.; this time is no greater than that expected from the slowness of instrument response.

Mixing in the Large Reaction Cell.—A small amount of acetone was injected into the cell which contained nitrogen at 1-atm. pressure, and the infrared absorption of the acetone was followed at 5.75 μ . The absorbance reached a constant value after 2.5 min. and did not change for at least 3 hr. thereafter.

(11) Wave length calibration was with methanol vapor taking $\nu_{OH} = 3682$ cm.⁻¹; A. Borden and E. F. Barker, *J. Chem. Phys.*, **6**, 553 (1938).

TABLE I
HALF-TIME FOR FORMATION OF KETO-ACETONE FOLLOWING
ILLUMINATION OF 2-PENTANONE^a

Pressure of 2-pentanone, mm.	Pressure of N ₂ , mm.	Illumination time, min.	No. of scans	Half-time, min. ^b	Nature of wall
0.18	0	2–10	31	2.19 ± 0.14	Al paint
0.18	750	2–10	18	3.31 ± 0.16	Al paint
0.18	750	3–11	23	3.38 ± 0.16	Al foil
0.36	750	3–10	31	3.33 ± 0.10	Al foil
0.36 ^c	750	5–10	16	3.65 ± 0.17	Al foil
0.36 ^d	750	5–10	7	3.89 ± 0.28	Al foil

^a Temperature usually 27°; *I*_a at lower pressures, $\sim 5 \times 10^{11}$ quanta/ml./sec. ^b The measure of precision is standard deviation throughout. ^c Corning 9863 filters. ^d Temperature 15°.

The half-life of ozone at room temperature and concentrations of about $5 \times 10^{-3}\%$ in 1 atm. of oxygen was measured by following the infrared absorption at 9.5 μ with an aluminum inner surface; under these conditions the half-life was 127 min. With the inner surface freshly coated with soot, the half-life was 2.3 min.

Formation of Acetone-*d*₁ on Photolysis of 2-Pentanone in Cells Treated with D₂O.—In addition to acetone-*d*₀, large amounts of acetone-*d*₁ and negligible (<2%) amounts of acetone-*d*₂ were formed when 2-pentanone was photolyzed in small cells pretreated with D₂O. The results are included in Table II. The run numbers show the order of performance. Several observations may be made from these data. (1) The ratios of acetone-*d*₁/acetone-*d*₀ were fairly reproducible, at least under the conditions of the control experiment performed occasionally to monitor any considerable changes in the system; compare runs 49, 52, 53, 55. (2) The ratio *d*₁/*d*₀ increased with decrease of incident intensity and concomitant increase of reaction time (conversion constant). (3) The ratio increased with time in the cell; that is, a high *d*₁/*d*₀ ratio was observed when the 2-pentanone was permitted to stand in the reaction cell for a time before illumination. (4) The *d*₁/*d*₀ ratio decreased with increase in conversion. (5) The *d*₁/*d*₀ ratio was about the same in a quartz cell as in a soft glass cell with quartz front window. (6) The presence of D₂O vapor in the cell increased the ratio of *d*₁/*d*₀. Under the most favorable conditions, 72% of the acetone was monodeuterated. (7) No exchange occurred during gas chromatographic separation of the acetone. (8) Acetone-*d*₁ formation was reduced when 1 mm. of D₂O vapor rather than 17 mm. was used in pretreatment. (9) The unconverted 2-pentanone from a photochemical experiment showed no more than 0.5% exchange. A mixture of acetone (3 mm.), 2-pentanone (10 mm.), and D₂O (17 mm.) was permitted to stand in the cell. Neither ketone showed more than 0.5% exchange in 12 hr.

Much less deuterium in the acetone product was observed following photolysis of 2-pentanone at 0.18 mm. pressure in the large aluminum-walled cell. The ratio of acetones *d*₁/*d*₀ was 0.06 or less, even with pretreatment of the cell for 36 hr. with D₂O vapor at 1.5-mm. pressure. The presence of 0.8-mm. D₂O during illumination did not appreciably increase the acetone-*d*₁ formation. Covering about 50% of the wall with glass likewise caused no increase in the *d*₁/*d*₀ ratio.

TABLE II

ACETONE EXCHANGE STUDIES IN THE PHOTOLYSIS OF 2-PENTANONE IN SMALL CELLS PRETREATED WITH D₂O*

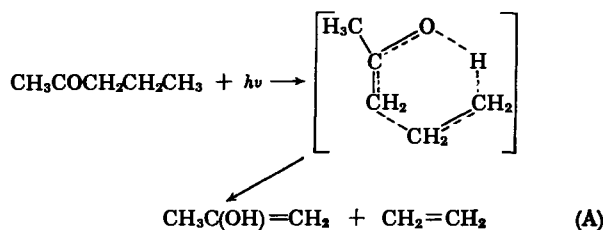
Run no.	Intensity of absorbed light	Photolysis time, min.	Time in cell before photolysis, min.	Acetone-d ₁ Acetone-d ₆	Remarks
49	I _a	30	5	0.17	All-quartz cell was used in runs 49-62
50	0.020I _a	1440	5	0.32	
51	0.058I _a	514	5	0.37	
52	I _a	30	5	0.25	Two 15-min. illuminations, each after 4-hr. standing
53	I _a	30	5	0.23	
54	I _a	15 + 15	240 + 255	0.65	
55	I _a	30	5	0.24	
56	I _a	30	484	0.40	
57	I _a	30	5	0.95	3 mm. of D ₂ O present in cell during illumination
58	0.162I _a	180	5	0.38	Conversion 40%
59	I _a	180	5	0.16	
60	0.092I _a	180	180	1.32	17 mm. of D ₂ O present in cell during illumination
61	I _a	30	5	0.19	Acetone separated by distillation
62	0.020I _a	720	5	2.42	17 mm. of D ₂ O present in cell during illumination; conversion 7%
63	I _a	30	5	0.25	Soft glass cell with quartz window
64	I _a	30	5	0.21	Soft glass cell with quartz window
65	I _a	30	5	0.13	Soft glass cell with quartz window; pretreatment with 1 mm. of D ₂ O rather than 17 mm. of D ₂ O as usual

* Temperature 27°; pressure of 2-pentanone, 12.2 mm.; I_a ~ 1 × 10¹⁴ quanta/ml./sec.; conversion usually constant at 15%

Formation of 1-Methylcyclobutanol.—This alcohol was a minor product under all conditions. Identification in the large cell experiments was by infrared absorption after separation by gas chromatography. The ratio of 1-methylcyclobutanol to ethylene formed in the large cell experiments was about 0.17; the ratio of 1-methylcyclobutanol to acetone in the small cells was about 0.07. In view of the uncertainties in amounts of the alcohol formed, these ratios may not be significantly different. Furthermore, conditions in the two sets of experiments were very different.

Discussion

Identification of the Enol-Acetone Primary Product in the Photolysis of 2-Pentanone.—On the basis of indirect evidence^{4,6} the mechanism of the Norrish "type II" primary process in ketone photolysis has been generally accepted to occur by way of a six-membered ring intermediate which involves bonding between a γ -hydrogen and the carbonyl oxygen. In the case of 2-pentanone this primary process is represented by (A). This work supports this view strongly.



Reported here are the first direct observations of the transient *enol*-acetone product of process A. A small absorption peak at 2.756 μ appears in the infrared spectrum of the irradiated 2-pentanone and disappears when the light is excluded. The only hydroxyl-containing compound which has been identified as a product of the gas phase photolysis of 2-pentanone, 1-methylcyclobutanol, cannot account for the absorption band; it absorbs at shorter wave lengths (2.73 μ) and is not a transient. It is reasonable to ascribe the 2.756 μ band to the H—O stretching vibration of the *enol*-acetone.¹² The delay in

(12) There are no published data of which the authors are aware on the free H—O stretching frequency of a simple *enol*. The spectra of some

the appearance of the *keto*-acetone band (half-time = 3.35 \pm 0.13 min.) coupled with the prompt appearance of the other product of process A, ethylene (half-time = 0.3 min.), proves that the *keto*-acetone is not formed initially as the finished molecule. The near equality of the half-time for *keto*-acetone formation and the *enol*-acetone disappearance (half-life = 3.34 \pm 0.11 min.) suggests strongly that the transient observed at 2.756 μ is indeed the *enol*-acetone.

The Mechanism of Enol-Acetone Conversion to Keto-Acetone.—The maximum concentration of *enol* obtainable at the steady state is limited by the incident light intensity and the pressure of 2-pentanone. The range of 2-pentanone pressure over which the half-time of acetone formation can be measured is limited at low pressures by the small amounts of acetone formed and at high pressures by the loss of sensitivity of the spectrometer due to strong background absorption by 2-pentanone. As a consequence of these limitations, the pressure of ketone could be varied only by a factor of two in these acetone half-time experiments. However, over this range the data of Table I show the half-time to be independent of 2-pentanone pressure (hence absorbed light intensity) for experiments with conditions otherwise the same. We may conclude from this evidence that the ketonization is first order in *enol*-acetone for our conditions.

The increase in the half-time for the *keto*-acetone appearance with decrease in temperature (see Table I) corresponds to an apparent activation energy of about 2 kcal./mole. A first-order vapor phase conversion of

members of a class of stable *enols* such as 1,2-dimesityl-1-propen-1-ol show an absorption at about 2.77 μ in chloroform solution (A. M. Buswell, W. H. Rodebush, and R. McL. Whitney, *J. Am. Chem. Soc.*, **69**, 770 (1947)). Considering the shift to higher frequencies expected in the vapor, this result would lead to expectation of a shorter wave length than 2.756 μ . However, our assignment of this band to the *enol*-acetone is in agreement with the trend toward longer wave lengths observed as the carbon system to which the hydroxyl is attached becomes more olefinic, as in the series: methanol, phenol, naphthol, and 9 phenanthrol. (See I. M. Hunsberger, R. Ketchum, and H. S. Gutowsky, *J. Am. Chem. Soc.*, **74**, 4839 (1952).) The absorption observed in liquid acetone at 3600 cm.⁻¹ and attributed to *enol*-acetone by J. Gerbier (*Compt. rend.*, **253**, 2210 (1961)) seems too strong to be due to a species present to the extent of 2.5 × 10⁻⁴% (G. Schwarzenbach and C. Wittwer, *Helv. Chim. Acta*, **30**, 669 (1947)). The band is probably due to traces of water hydrogen bonded to acetone (P. J. Lucchesi, *J. Am. Chem. Soc.*, **78**, 4229 (1956)).

enol- to *keto*-acetone would be expected to have an activation energy considerably greater than this. A ketonization on the cell surface seems to be more probable. The half-life of ozone in the carbon-coated vessel provides an upper limit of 2.3 min. for the half-time of convective transport of a trace component to the wall at a total pressure of 1 atm. Since the ozone-carbon reaction is probably not of perfect collision efficiency, the true time required may be much shorter. Transport times may affect neither the half-life of *enol* nor the half-time for *keto* appearance.

In terms of this picture, the slight increase in half-time for appearance of *keto*-acetone in experiments in which the incident light was filtered may arise from a slight reduction in surface heating by elimination of the visible radiation from the mercury arcs.

If ketonization at the wall is the dominant mode of *enol*-acetone destruction, then deuterium-hydrogen exchange may accompany the process when groups -OD are present at the wall. The previous indirect evidence for the formation of *enol*-acetone in the type II process was obtained from such experiments. Srinivasan⁶ examined in detail the hydrogen-deuterium exchange between the surface and acetone formed in 2-hexanone photolysis. He found an increase in the per cent of exchange as the intensity was decreased (and consequently the reaction time was increased). He interpreted this result as an indication that part of the ketonization took place as a gas phase reaction between two *enol* molecules.

We have carried out very similar experiments with 2-pentanone to test for this mechanism of *enol* disappearance. These findings are summarized in Table II. Since the per cent exchange is a function of the extent of 2-pentanone decomposition, the per cent decomposition was held constant in most runs. In confirmation of Srinivasan's observations, the data show an apparent trend of increased deuteration of the acetone at lowered intensity. However, the effect is related, at least in part, to the total time which the run consumed; permitting the 2-pentanone to stand for a time in the pretreated cell before illumination enhances the deuterium content of the acetone product. Compare runs 53 and 54, Table II.

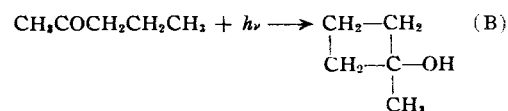
Since the per cent exchange is dependent on the per cent conversion as well as the time in the cell, the true intensity effect, if any, cannot be studied unambiguously. It appears, however, that the enhancement of exchange, apparently due to intensity reduction, can be accounted for by the simultaneous increase of time in the cell. These results therefore provide no evidence for the gas phase bimolecular destruction of *enol*. It should be pointed out that the "time-in-cell" effect is not simply due to nonphotochemical exchange with the ketones; this is negligible. Rather, the explanation probably must come from consideration of these and other facts: first, the observation of water in the chromatograms of the cell contents; second, the enhancement of exchange when D₂O was intentionally mixed with 2-pentanone before photolysis; third, the very small extent of exchange observed in the large cell experiments, even with 0.8 mm. of D₂O present. The third observation seems to rule out the possibility that

the exchange of D₂O with *enol* may occur as a gas phase reaction, but this cannot be excluded from the results of the experiments with small cells alone. We suppose that the pretreatment with D₂O vapor involves not only deuteration of silanol ($\equiv\text{SiOH}$) and weak adsorption of D₂O, but also some strong adsorption of D₂O, not entirely removed during final evacuation. Over the course of an illumination, or upon standing before illumination, the D₂O is gradually discharged into the vapor phase. During photolysis, it may either exchange on the wall with *enol* or may serve to redeuterate silanol sites that had lost deuterium to *enol*.

The only slight exchange observed in the large tank, even following extensive treatment with D₂O vapor, is surprising in view of the probability of wall ketonization. The aluminum may not be a suitable surface for the exchange; however, soft glass is a suitable surface (Table II), and partly lining the cell with soft glass did not increase exchange appreciably. The lack of appreciable exchange in the large cell may be reconciled with wall ketonization by supposing that ketonization can occur on an aluminum surface without exchange and that ketonization is much slower on glass than on aluminum. In this last case, the half-life of *enol* would be increased in the partly glass-walled vessel. The data do suggest this (half-life = 4.7 ± 0.3 min.) but only three half-life measurements were made in the hybrid vessel, so the matter is not settled unambiguously.

In view of all the evidence at hand we would conclude that the dominant mode of transformation of *enol*-acetone involves reaction at the wall of the vessel; depending on the nature of the wall the process may or may not involve exchangeable hydrogen atoms at the surface.

The Formation of 1-Methylcyclobutanol in 2-Pentanone Photolysis.—The conditions required for the formation of cyclic alcohols in the vapor-phase photolysis of ketones containing γ -hydrogen atoms are not completely clear. The evidence regarding the occurrence of these compounds among the products is conflicting.¹³⁻¹⁵ Our results confirm the occurrence of process B in the vapor phase photolysis of 2-pentanone, but the experiments with the small D₂O treated cells indicate a somewhat lower quantum yield than would be expected from the results of Ausloos and Rebbert¹³ in untreated cells. We believe that the failure of some



workers to detect the cyclobutanol products is due in part to destruction of these alcohols during gas chromatographic analysis.

Acknowledgment.—The authors are grateful for the support given this work by grants from the Division of Air Pollution, Bureau of State Services, U. S. Public Health Service.

(13) P. Ausloos and R. E. Rebbert, *J. Am. Chem. Soc.*, **83**, 4897 (1961).

(14) J. L. Michael and W. A. Noyes, Jr., *ibid.*, **85**, 1027 (1963).

(15) J. N. Pitts, Jr., and A. D. Osborne, "Chemical Reactions in the Lower and Upper Atmosphere," Interscience Publishers, Inc., New York, N. Y., 1961, p. 129.