be plotted against $\mu^{1/2}_+ + 3\mu^{1/2}_-$ rather than against the ordinary ionic strength. Such a plot is shown in Fig. 4. It is apparent that the data can be fitted within the limits of experimental error by a single curve. For the present this method of plotting the data must be considered as purely empirical although it was suggested by some theoretical considerations.

The analysis of the effect of temperature on the quenching process is complicated by the fact that the quenching constant is the product of the lifetime of the excited molecule and a bimolecular rate constant. If the lifetime is constant the entire temperature effect is that on the bimolecular rate constant. Then a straight line should be obtained if the logarithm of the quenching constant is plotted against the reciprocal of the absolute temperature. We found that with both the systems studied in this paper such a plot yields a curved line. Such a curvature could be caused by a variation of the lifetime with temperature. Actually, Lewschin[6] has reported that the fluorescence yield from solutions of fluorescein decreases as the temperature is raised. A decreased yield can be caused by the lifetime being decreased by an increase in the rates of the competing first order reactions. It is possible now to measure lifetimes of solutions such as these with sufficient accuracy to test such an explanation; therefore, we shall defer further discussion of the temperature effects until such measurements are available.

The conclusions which may be drawn from the data we have presented are not as definite as we had hoped that they might be. Certainly the fit with the straight line based on the Debye–Hückel theory, which is shown in Fig. 2, must be taken as support for the equation based on that theory, although it does not necessarily confirm the physical interpretation put on the parameters. On the other hand, the curves shown in Fig. 3 and Fig. 4 indicate that specific effects are less pronounced if stress is laid on the effect of ions of opposite sign to those under consideration. On the basis of our experience we would say that rate constants determined in solutions of variable ionic constitution can be correlated best by plots of the type shown in the latter figures.

BERKELEY, CALIFORNIA

[6] W. L. Lewschin, *Z. physik*, **43**, 230 (1927).

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES, NORTHWESTERN UNIVERSITY]

Structure and Reactivity in the Vapor-Phase Photolysis of Ketones. I. Methyl Cyclopropyl Ketone[1,2]

BY J. N. PITTS, JR., AND I. NORMAN

RECEIVED MARCH 24, 1954

The vapor-phase photolysis of methyl cyclopropyl ketone at 2654–2537 Å. leads primarily to rearrangement giving methyl propenyl ketone with a quantum yield of 0.31 ± 0.02 from 25 to 120°. The probability of dissociation of the parent ketone into radicals must be small, since the quantum yield of carbon monoxide is only 0.12 at 170°. Minor non-condensable products are 1-butene, propylene, ethane, methane, ethylene and biallyl and, for the runs above 100°, traces of cyclopropane. A reaction sequence is proposed that accounts for the olefinic nature of the non-condensable products, and the formation of the α,β-unsaturated ketone.

In recent years it has become increasingly evident that the structures of alkyl substituents have a pronounced effect upon the primary modes of photodecomposition of simple aliphatic ketones.[3] It is now recognized that all simple aliphatic ketones photodissociate to some extent by a Norrish Type I free radical process[4] to give alkyl and acyl radicals. Acetone,[3b,5] methyl ethyl ketone,[6–8] and diethyl ketone[9] decompose almost exclusively in this manner. However, ketones with larger alkyl groups, such as methyl *n*-propyl ketone,[3b] di-*n*-propyl ketone,[10] and methyl *n*-butyl ketone,[11] also react to a significant extent by an intramolecular rearrangement that gives a lower ketone and an olefin. The relative probabilities of dissociation of the bonds adjacent to the carbonyl chromophore also seem to depend upon the nature of the substituents. For example, in the photolysis of methyl ethyl ketone at 3130 Å. the primary split into ethyl and acetyl radicals is highly favored over the competing process that yields methyl and propionyl radicals.[6,8,12]

In view of these results it seemed worthwhile to initiate a study of the vapor-phase photolysis of several types of relatively simple ketones having cycloalkyl or alkenyl substituents. An attempt is now being made to evaluate the influence of these types of substituents on primary processes, and to study the secondary reactions of the radicals produced therein. This paper presents the results obtained from a study of the photolysis of methyl cyclopropyl ketone at 2654–2537 Å. and temperatures from 25 to 170°.

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[1] Presented at the Los Angeles Meeting of the American Chemical Society, March, 1953.

[2] Taken from the doctoral dissertation of I. Norman, Northwestern University, 1953.

[3] See the comprehensive reviews. (a) W. Davis, Jr., *Chem. Revs.*, **40**, 201 (1947); (b) A. J. C. Nicholson, *Rev. Pure and Applied Chem.*, **2**, 174 (1952).

[4] R. G. W. Norrish and M. E. S. Appleyard, *J. Chem. Soc.*, 874 (1934).

[5] W. A. Noyes, Jr., and L. M. Dorfman, *J. Chem. Phys.*, **16**, 788 (1948).

[6] V. R. Ells and W. A. Noyes, Jr., THIS JOURNAL, **61**, 2492 (1939).

[7] W. J. Moore and H. S. Taylor, *J. Chem. Phys.*, **8**, 466 (1940).

[8] J. N. Pitts, Jr., and F. E. Blacet, THIS JOURNAL, **72**, 2810 (1950).

[9] K. O. Kutschke, M. J. H. Wijnen and E. W. R. Steacie, *ibid.*, **74**, 714 (1952).

[10] C. R. Masson, *ibid.*, **74**, 4731 (1952).

[11] W. Davis, Jr., and W. A. Noyes, Jr., *ibid.*, **69**, 2513 (1947).

[12] G. R. Martin and H. C. Sutton, *Trans. Faraday Soc.*, **48**, 823 (1952).

Experimental

The photochemical apparatus was similar to the type first developed by Blacet and Heldman[13] but embodied several significant changes. A quartz reaction cell, 30-mm. diameter by 200-mm. long, was set in an air-thermostated masonite chamber capable of being heated to 170° and controlled to about ±1° by a Fenwal Thermoswitch. The sample introduction system could be heated electrically to about 80° to provide a suitable pressure of the ketone. A Hanovia Type A Alpine Burner operating on alternating current was employed with a gaseous bromine–chlorine filter (5-cm. length, Hanovia Mfg. Co., Newark, N.J.) and suitable lenses and stops so arranged that a slightly diverging beam of radiation almost filled the cell. The volume of the illuminated region was about 131 cc. A 1P28 photomultiplier detector unit was attached to the exterior of the masonite chamber. In order to achieve linearity of operation the radiation was attenuated by means of a pin hole diaphragm at the end of the cell. In addition to the strong ultraviolet lines at 2654 and 2537 Å. (the 2654 Å. radiation was approximately twice as intense as the 2537 Å.), the filter transmitted considerable visible radiation. This was eliminated by placing just in front of the phototube a 3-mm. thickness of Corning 9863 red-purple corex glass and a water-jacketed cell of one inch path length containing a solution of $CoSO_4 \cdot 7H_2O/NiSO_4 \cdot 6H_2O$ (276 and 86.8 g./liter, respectively).

Methyl cyclopropyl ketone[14] (E. C. Matheson and Company), previously stored over drierite, was distilled in a nitrogen atmosphere. The reflux ratio was about 40:1 in the "forty plate" Podbielniak high temperature fractionating column. The center cut (b.p. 110.2–110.4°, 745 mm.) was distilled *in vacuo* into the ketone reservoir of the heated inlet system and a center cut was again retained. Mass spectrometric analysis of this sample showed no significant quantities of contaminants of higher molecular weight. The diethyl ketone and acetone used were reagent grade (Matheson and Mallinckrodt Co., respectively) and were dried and distilled in the same manner as the methyl cyclopropyl ketone.

Diethyl ketone at 25° and 30 mm. pressure was employed as an internal actinometer. A separate gas train was used to avoid contamination of the methyl cyclopropyl ketone system. The quantum yield of carbon monoxide was taken to be 0.65, from the data of Kutschke, Wijnen and Steacie.[9] The reliability of this actinometer system was verified in two photolyses of acetone at 120° from which values of 0.96 and 1.00 were obtained for Φ CO.

All quantum yield runs were carried 1–5% to completion. The non-condensable gases were separated with the aid of a Toepler pump from the condensable products and unreacted ketone at −79°. The gas sample was transferred to a Blacet–Leighton apparatus where it was treated for two minutes with a porous bead saturated with concentrated phosphoric acid to remove the major portion of any unreacted ketone pumped over with the products. This was followed by a potassium hydroxide bead to remove excess acid and water vapor, and finally by silver oxide to determine carbon monoxide. The residual gases were then separated into two aliquot portions, one of which was analyzed for total hydrocarbons on a Westinghouse Type LV mass spectrometer,[15] and the other for total olefins on the Blacet–Leighton apparatus using the hydroxymercurial method of Pyke, Kahn and LeRoy.[16] Tests on known synthetic samples showed that cyclopropane was not removed by the mercuric acetate-mercuric nitrate bead. Thus, in those analyses where the trace amounts of cyclopropane were to be determined the mass spectra were simplified by removing the olefins chemically prior to running the samples on the mass spectrometer.

The bathochromic shift in the ultraviolet absorption spectrum of methyl propenyl ketone made it a straightforward matter to analyze quantitatively for this α,β-unsaturated ketone in the presence of a large excess of the unreacted substrate. The condensable fraction from a run was taken up in 10.0 ml. of isoöctane and the optical density of the resulting solution determined at 3300 Å. with a Beckman Model D.U. spectrophotometer. The concentration of product was then estimated from a graph giving concentration of methyl propenyl ketone *vs.* optical density. For each run in which spectrophotometric determinations of total molecules of methyl propenyl ketone were carried out, the number of molecules of carbon monoxide was determined concurrently. From these data and the previously established values for Φ CO at each temperature, the quantum yields of methyl propenyl ketone were readily calculated.

Experimental Results

The Non-condensable Products.—Surprisingly low yields of gaseous products were obtained in the photolysis of this ketone. The quantum yield of the major product, carbon monoxide, was only 0.12 at 170°. Other products identified were 1-butene, propylene, ethane, methane, ethylene, diallyl and traces of cyclopropane in the 120 and 170° runs. The quantum yields as a function of temperature at 2654–2537 Å., and a constant concentration of about 1.02 millimoles per liter, are presented in Table I.

TABLE I

THE EFFECT OF TEMPERATURE ON THE QUANTUM YIELDS OF THE GASEOUS PRODUCTS AT 2654–2537 Å.

Temp., °C.	25	60	100	120	170
Experiment	23	27	28	21	22
Pressure, mm.	18.5	21.2	23.5	25.0	28.0
Intensity, (quanta/sec.) × 10^{-15}	1.85	1.94	1.93	1.85	1.85
Fract. absorbed, *Qm*	0.549	0.560	0.581	0.610	0.613
Time, sec. × 10^{-4}	7.74	2.16	2.07	1.44	2.16
Quantum yields, Φ, × 10^2					
Carbon monoxide	3.9	5.0	6.2	8.6	11.8
1-Butene		2.1	...	3.8	3.4
Propylene		0.5	...	1.8	2.8
Ethane		0.8_7	0.8_4	1.6	0.6_1
Methane		0.3_4	1.1	2.0	6.2
Ethylene		0.2	...	0.7	0.7
Biallyl[a]		0.06	...	0.1	0.2
Cyclopropane		0.00	...	trace	0.3
Total unsaturates determined chemically	2.3	3.0	...	6.3	7.1

[a] These are only approximate yields

At −79° biallyl has a relatively low vapor pressure and a quantitative separation of it from the condensed phase could not be achieved by means of the Toepler pump. Thus the reported quantum yields are significantly low. Although cyclopropane was a product at 120 and 170° it was present to the extent of 1% or less of the total gaseous fraction and no accurate estimation of its yield could be made. A dark run at 170° for six hours gave no detectable products in either phase.

The Condensable Products.—Several fifty-hour photolyses were carried out in order to form sufficient quantities of the condensable products to be detected in the presence of the large excess of ketone. The results can be summarized as follows.

Spectrophotometric Analysis.—Characteristic absorption maxima appeared at 13.9 and 6.17μ in the infrared spectrum of the irradiated ketone. The duplication of this "unknown spectrum" by that of a synthetic sample, consisting of a mixture of *cis* and *trans* methyl propenyl ketone[17] in methyl cyclopropyl ketone, was good evidence that this

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[13] F. E. Blacet and J. D. Heldman, THIS JOURNAL, **64**, 889 (1942).

[14] The earliest samples used were kindly furnished by Professors G. Hammond and R. P. Mariella.

[15] The authors are deeply indebted to Dr. Wayne Bell for determining the mass spectra.

[16] R. Pyke, A. Kahn and D. J. LeRoy, *Ind. Eng. Chem., Anal. Ed.*, **19**, 65 (1947).

[17] Kindly prepared by Dr. John Patterson.

α,β-unsaturated ketone was the only "condensable" product formed in appreciable quantities. Examination of the infrared spectrum of the pure *trans* ketone[17] revealed the fact that the peak at 13.9μ in the mixture was due solely to the *cis* isomer. Unfortunately a spectrum of the pure *cis* compound was not available and at the time this work was carried out no unequivocal means could be devised for determining the relative quantum yields of the two isomers.

The formation of methyl propenyl ketone was further verified when ultraviolet absorption spectra of the condensates showed two maxima, one at 2750 Å. due to the ketone substrate, and the other at about 3250 Å. Spectra of known synthetic mixtures confirmed the fact that the latter peak was characteristic of α,β-unsaturated methyl ketones and this fact served as the basis for the analytical procedure for this product. The results for the quantum yields of methyl propenyl ketone as a function of temperature appear in Table II.

TABLE II

QUANTUM YIELDS OF METHYL PROPENYL KETONE AS A FUNCTION OF TEMPERATURE AT 2654–2537 Å.

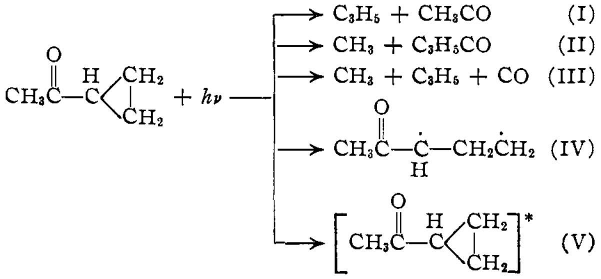
Temp., °C.	25	60	100	120	170
Optical density of condensable fraction	0.083	0.055	0.077	0.052	0.051
Molecules $CH_3COCH{=}CHCH_3 \times 10^{-18}$	21.7	15.7	20.6	14.8	14.5
Molecules CO $\times 10^{-18}$	2.83	2.34	4.06	3.96	4.42
Φ CO	0.039	0.050	0.062	0.086	0.118
Φ $CH_3COCH{=}CHCH_3$	0.30	0.34	0.31	0.32	0.39

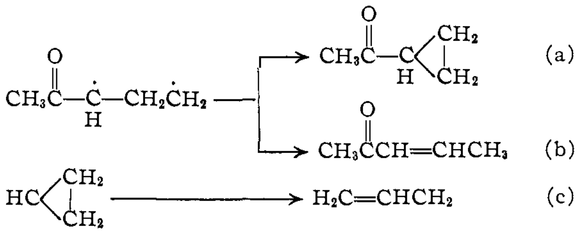
Mass Spectrometric Analysis.—An appreciable peak at *m/e* 86 in the condensate from a photolysis at 25° was absent in a similar run at 170°. By analogy with the well established acetone photolysis it seems reasonable to assume this peak represented the parent mass of biacetyl; however its identity was not established unequivocally. Slight increases in relative intensities at *m/e* 82, 81, 68, 67, 54, 41, 39 and 27 corresponded to contributions from the biallyl which was not pumped over with the non-condensables. A quantitative estimate of the diene remaining in the condensables was not attempted. Other small differences in the mass spectra of the products and the parent ketone were ascribed to the methyl propenyl ketone known to be present.

Discussion of Results

The following sequence of reactions is presented as one possible means of explaining the observed products of the photolysis of methyl cyclopropyl ketone, and the effect of temperature on their rates of formation.

Primary Processes and "Fast" Rearrangements

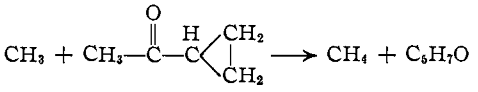


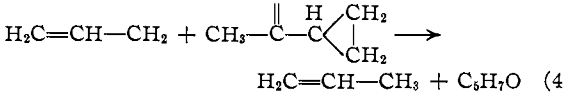


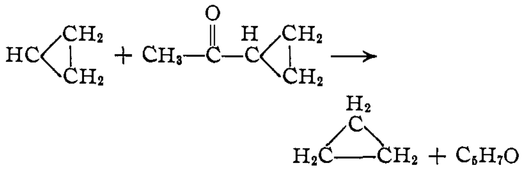
Secondary Reactions

$$CH_3CO \longrightarrow CH_3 + CO \quad (1)$$

$$C_3H_5CO \longrightarrow C_3H_5 + CO \quad (2)$$


(3)


(4)


(5)

$$CH_3 + H_2C{=}CH{-}CH_2 \longrightarrow H_2C{=}CH{-}CH_2{-}CH_3 \quad (6)$$

$$CH_3 + CH_3 \longrightarrow C_2H_6 \quad (7)$$

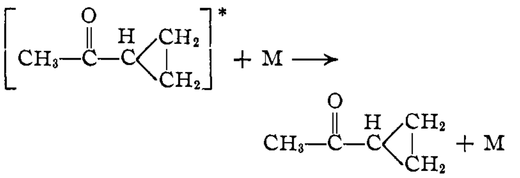
$$2H_2C{=}CH{-}CH_2 \longrightarrow H_2C{=}CH{-}CH_2{-}CH_2{-}CH{=}CH_2 \quad (8)$$

Secondary Reactions

$$2CH_3CO \longrightarrow (CH_3CO)_2 \quad (9)$$

$$R + C_5H_7O \longrightarrow RC_5H_7O \quad (10)$$

$$R + CH_3CO \longrightarrow RCOCH_3 \quad (11)$$


(12)

Primary Processes: Primary Processes (I), (II) and (III).—These primary processes giving monoradicals must be of low probability since Φ CO at 170° is only 0.12; acetone,[5] methyl ethyl ketone,[18] and diethyl ketone[9] give yields close to unity under reasonably comparable conditions.

The formation of only trace quantities of cyclopropane in contrast to the relatively much larger amounts of 1-butene, propylene and biallyl suggests that *if* cyclopropyl radicals are formed in reactions I, III or 2, they must rearrange rapidly to the more stable allyl structure (reaction c). A "fast" rearrangement of this type has also been postulated by Gunning[19] to explain the results of recent work on the mercury photosensitized decomposition of cyclopropane. There is no experimental evidence as to the precise structure of the C_3H_5CO radical formed in II. It may retain the cyclopropyl ring structure, it may exist as the α,β-

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[18] J. N. Pitts, Jr., Doctoral Dissertation, University of California, Los Angeles, 1949.

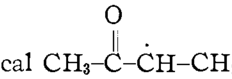
[19] H. E. Gunning, private communication.

unsaturated acyl radical, or it might be present in both forms. In any case, it is evident that the dissociation products of this acyl radical ultimately appear almost entirely as olefins and carbon monoxide. In the absence of data from photolyses in the presence of inhibitors further speculation on the structure of this radical and on the primary quantum yields of I, II and III seems unwarranted. It should also be recognized that, on the basis of evidence to date, one cannot completely rule out the possibility of a concerted primary process giving directly carbon monoxide and 1-butene. However, by analogy with other ketones such an intramolecular process seems unlikely.

Primary Processes (IV), (V).—No direct experimental evidence was obtained for primary process (IV). However, it is convenient to postulate a biradical intermediate in explaining two important experimental facts, the low over-all yield of gaseous products and the formation of relatively large amounts of methyl propenyl ketone in a process independent of temperature over the range 25–120°.

The formation of the biradical requires the breaking of a carbon–carbon bond *beta* to the carbonyl chromophore. However, this seems reasonable considering the strain present in a cyclopropyl ring, and in view of the fact that the current estimate for the carbon–carbon bond dissociation energy in cyclopropane is only about 57–60 kcal./mole.[20] This is considerably less than the value of 72 kcal./mole calculated for D(C–C) in acetone.[3b] Both bond dissociation energies are of course much less than 108 kcal./mole, the energy corresponding to 2654 Å. radiation. Actually, in the case of methyl *n*-butyl ketone,[11] and di-*n*-propyl ketone,[10] C–C bonds *beta* to the carbonyl are readily broken when quanta of 3130 Å. radiation (91 kcal./mole) are absorbed by the molecule. However, in the latter cases the ultimate products of this temperature-independent type of process are acetone and propylene, and acetone and ethylene, respectively.

Short-lived biradicals have been suggested as intermediates in a variety of reaction systems. Bawn and Hunter[21] employed the sodium diffusion flame technique with 1,3-dibromopropane and found cyclopropane was produced in a homogeneous gas reaction. They postulated that it was formed by the cyclization of trimethylene biradicals generated in the "flame." Further indirect evidence has come from several studies on the photolysis of the cyclic ketones[22-25] and on the pyrolysis of terpenes.[26] As a result of these investigations, various reaction sequences have been proposed in which biradicals formed in primary processes, either photochemical or thermal, are considered to undergo fast cyclization or hydrogen atom transfer reactions.



If the biradical $CH_3-\overset{\overset{O}{\|}}{C}-\dot{C}H-CH_2-\dot{C}H_2$ is formed by IV then the very low over-all yield of gaseous products and the formation of methyl propenyl ketone can be explained on the basis that IV has a much greater probability than I, II and III combined, and that the two most probable reactions of the biradical are recyclization a, and rearrangement b. The fact that the quantum yield of methyl propenyl ketone formation is independent of temperature over the wide range from 25 to 120°, indicates that a and b are fast relative to the usual thermal combination and abstraction reactions of monoradicals. Also, the relatively large yields of methyl propenyl ketone point to a rate of hydrogen atom transfer in the biradical, b, that is at least comparable to the rate of recyclization, a, and perhaps much faster.

It is evident that at 120° the sum of the yields for decomposition and rearrangement adds up to only about 0.4. Thus, about 60% of the molecules that absorb radiation do not undergo permanent change; instead, they lose the energy by either, or both, of the sequences IV–a, V–12, or by some internal degradation of energy.[10,27] However, in the absence of data on pressure effects or fluorescence yields, it is not possible to evaluate the magnitudes of these individual processes.

The possibility also exists of a primary process in which a C–C bond γ to the carbonyl is broken and methyl isopropenyl ketone is formed. The close agreement between the infrared spectra of the photolysis products and that of a synthetic mixture of *cis* and *trans* methyl propenyl ketone indicates that the isopropenyl isomer must be formed in very small amounts, if at all.

Secondary Reactions.—Some of these processes are postulated to explain the products observed and the temperature dependence of their rates of formation while others are proposed on the basis that they seem reasonable when compared with analogous reactions known to occur in the photolysis of other ketones.

Processes 1, 2 and III are suggested to account for the formation of carbon monoxide. Although the activation energy for acetyl decomposition is reported to be 13.5 kcal./mole[28] no value is available for C_3H_5CO. Until the structure of this radical is determined, discussion of the relative rates of 1 and 2 seems unwarranted.

The formation of methane and propylene can be explained on the basis of the hydrogen abstraction reactions 3 and 4, while 1-butene, ethane and biallyl are thought to be the result of radical combinations 6, 7 and 8. Although the very small yields of the gaseous products preclude a detailed kinetic analysis of the results, an approximate value for

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[20] F. Seubold, *J. Chem. Phys.*, **21**, 1616 (1953). In this paper the value of 50 kcal./mole is given but, in later calculations, Dr. Seubold used a more recent set of electron impact data and revised D(C-C) upwards about 7–9 kcal./mole.

[21] C. E. H. Bawn and R. F. Hunter, *Trans. Faraday Soc.*, **34**, 608 (1938).

[22] O. D. Saltmarsh and R. G. W. Norrish, *J. Chem. Soc.*, 455 (1935).

[23] C. H. Bamford and R. G. W. Norrish, *ibid.*, 1521 (1938).

[24] S. W. Benson and G. B. Kistiakowsky, THIS JOURNAL, **64**, 80 (1942).

[25] A. Miller, Doctoral Dissertation, Univ. of California, Los Angeles, 1952.

[26] A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," John Wiley and Sons, Inc., New York, N. Y., 1953.

[27] C. H. Bamford and R. G. W. Norrish, *J. Chem. Soc.*, 1505 (1935); 1531, 1544 (1938).

[28] D. H. Volman and W. M. Graven, *J. Chem. Phys.*, **20**, 919 (1952).

$E_3 - {}^1/_2\, E_7$ of 9.6 ± 1 kcal./mole for the range 60 to 170° was calculated by the method of Noyes and Dorfman.[5] This might be compared to values from 9.5 to 9.7 kcal./mole obtained for methyl attack on acetone.[29] In view of the uncertainty in the quantum yields of formation of diallyl, it does not seem profitable at this time to attempt to evaluate E_4. However, it would seem qualitatively that because of the resonance energy associated with an allyl radical compared to methyl,[30,31] E_4 should be considerably greater than 9.6 kcal./mole. Reaction 5 was included in the mechanism to account for the traces of cyclopropane detected at elevated temperatures.

It is evident from the temperature dependence of the quantum yields of 1-butene, ethane and biallyl that the combination reactions 6, 7 and 8 have activation energies much less than the hydrogen abstraction processes. Actually E_7 is known to be of the order of 0.0 to -1.6 kcal./mole[32,33] and it seems likely that E_6 and E_8 are also close to zero.

The formation of biacetyl, which is indicated by the mass spectrometric evidence, occurred, presumably by 9, at 25° but not at 170°. A similar effect has been well known in acetone photolysis[5] and explained on the basis that the acetyl radical dissociates rapidly by 1 at temperatures above 100°. There is no evidence to date as to whether or not a specific hydrogen atom is removed by radical attack on the parent ketone. Thus, the product of the abstraction processes 3, 4 and 5 has been designated simply as C_5H_7O. At temperatures above 100° R may represent methyl, allyl or C_5H_7O radicals and it is clear that a number of products could be formed by 10. In photolyses carried out near room temperatures the situation is further complicated by the fact that acetyl radicals also probably combine with other radicals, R, as indicated in 11. A very complex mixture of reaction products would be expected to result from 9, 10 and 11, and in view of the very low yields no detailed effort was made to determine each of them.

No "simple" primary or secondary reaction could be devised to explain the ethylene formed. It is interesting to note, however, that Mandelcorn and Steacie[34] also found significant quantities of ethylene in the products of the high temperature photolysis of acetone.

Acknowledgment.—The authors are indebted to the Atomic Energy Commission for generous support through contract AT(11-1)-89, Project No. 4. One of us (I. Norman) was also supported in part by an Eastman Kodak Fellowship and by a grant from the Abbott Fund of Northwestern University.

EVANSTON, ILLINOIS

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[29] For a comprehensive review see "The Reactions of Methyl Radicals," by A. F. Trotman-Dickenson, *Quart. Rev.*, **VII**, 198 (1953).

[30] M. Szwarc and A. H. Sehon, *J. Chem. Phys.*, **18**, 237 (1950).

[31] D. P. Stevenson, private communication, 1953.

[32] R. Gomer and G. B. Kistiakowsky, *J. Chem. Phys.*, **19**, 85 (1951).

[33] K. U. Ingold and F. P. Lossing, *ibid.*, **21**, 1135 (1953).

[34] L. Mandelcorn and E. W. R. Steacie, *J. Can. Res.*, in press.

[CONTRIBUTION FROM THE MOORE LABORATORY OF CHEMISTRY, AMHERST COLLEGE]

Differential Capacity of Mercury in Aqueous Sodium Fluoride Solutions. I. Effect of Concentration at 25°

BY DAVID C. GRAHAME

RECEIVED APRIL 3, 1954

The differential capacity of mercury in contact with aqueous solutions of sodium fluoride has been studied as a function of concentration at 25°. The results show that from the capacity measurements at any one concentration (but preferably a high one) it is possible to calculate the capacity at all others. This result confirms an hypothesis advanced earlier to the effect that in the absence of specific adsorption the differential capacity of the region lying between the metal and the outer Helmholtz plane depends upon the surface charge density of the metal but not upon the concentration of the electrolyte. The results serve as an additional strong confirmation of the classical theory of the diffuse double layer. They also provide data which can be used for an exacting test of the accuracy of techniques used for the experimental measurement of the differential capacity of the electrical double layer.

The electrocapillary properties of aqueous solutions of fluorides are of special interest because it has been shown[1] that the fluoride ion is unique (in so far as is now known) in that it is not chemisorbed on mercury at 25° even when the latter is positively charged except, perhaps, when the positive charge becomes rather large. Solutions of *sodium* fluoride are particularly convenient for these studies because of the nearly equal mobilities of the ions, which makes for small and reproducible liquid junction potentials.

Some early studies on the differential capacity of aqueous solutions of sodium fluoride on mercury have already been reported from this Laboratory,[2] but it was emphasized that the measurements were of a preliminary nature, having been made before the techniques of measurement had been fully worked out. It also happens that solutions of sodium fluoride give less reproducible results than most other simple electrolytes, probably because of the greater difficulty associated with the purification of this salt, and because it is less pure to begin with as well. In the present work sufficient purity has been achieved to reduce the errors arising on this account to negligible proportions.

The results to be reported here will be treated in the same theoretical manner as those reported earlier.[2] It will be shown that experiment and theory now agree very satisfactorily except in the most dilute solution studied and except at strongly anodic potentials, where the theory is not expected to ap-

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[1] D. C. Grahame and B. A. Soderberg, *J. Chem. Phys.*, **22**, 449 (1954).

[2] D. C. Grahame, *Chem. Revs.*, **41**, 441 (1947).