It is believed that our failure to detect KZn_4 is attributable to the very slow rate of reaction between zinc and potassium owing to the low concentrations of potassium solutions employed. Both Kraus and Kurtz and Burgess and Rose used much more concentrated metal solutions.

Figure 2 shows that cadmium(II) iodide is reduced directly to elemental cadmium (calcd., 14.9 ml.; found, 15.0 ml.) which was confirmed by X-ray diffraction patterns. If this reaction proceeds through the intermediation of Cd^{1+}, this species is not detectable by the method used. The slow secondary reaction shown by Fig. 2 apparently leads to the formation of KCd_3 (calcd., 17.5 ml.; found, 17.9 ml.), which was confirmed by the back-titration method illustrated by Fig. 3 (calcd. for KCd_3, 22.2 ml.; found, 21.9 ml.). These and several related titrations that employed modified procedures (but which are not reported in this paper) provided no evidence whatever for the compounds KCd_7 and KCd_{11} previously reported.[17]

Although the titration of mercury(II) iodide with potassium (Fig. 4) shows only the 2-electron reduction to elemental mercury (calcd., 15.1 ml.; found, 14.5 ml.), which was confirmed by the identification of this product, the titration of potassium with mercury(II) iodide solution (Fig. 5) gives evidence of the formation of KHg (calcd., 15.8 ml.) and KHg_2 (calcd., 19.6 ml.), both of which are known compounds.[18] Further confirmation of the formation of KHg, but not KHg_2, was obtained from the experiments in which mercury(II) iodide was reduced with excess potassium followed by back-titration with ammonium iodide solution. In these cases, as well as in titrations involving the reduction of cadmium(II) iodide, it was observed that the identity of the specific intermetallic compounds detected is quite sensitive to the conditions prevailing, particularly concentration. In order to obtain reproducible stoichiometry, it is necessary to control all conditions within a rather narrow range.

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[17] D. T. Smith, *Z. anorg. Chem.*, **56**, 119 (1908).

[18] J. W. Mellor, "Comprehensive Treatise on Inorganic and Theoretical Chemistry," Vol. IV, Longmans, Green and Co., New York, N. Y., 1923, p. 1015.

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF NORTHWESTERN UNIVERSITY]

Structure and Reactivity in the Vapor Phase Photolysis of Ketones. II. Methyl Neopentyl Ketone[1]

BY T. W. MARTIN AND J. N. PITTS, JR.[2]

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The major products of the vapor phase photolysis of $MeCOCH_2CMe_3$ from 120 to 250° at 3130 and 2654 Å. are isobutylene and acetone in amounts that are nearly equivalent, and virtually independent of temperature and wave length. The quantum yield, Φ, of isobutylene at 3130 Å. is 0.23 and 0.27 at 120 and 250°, respectively. Φ_{CO} under the same conditions increases from 0.04 to 0.17. Other minor non-condensable products are CH_4, C_2H_6, Me_3CH and Me_4C. A mechanism is proposed in which the major products arise directly from a primary intramolecular process, whereas the minor products come from secondary thermal reactions of radicals formed in several free radical primary processes. $MeCOCH_2CHMe_2$ also photodissociates chiefly into acetone and an olefin, in this case propylene. It is proposed that this type of process is general for aliphatic ketones having γ-hydrogen atoms and that the efficiency of the process can be correlated with the structure of the ketone and its characteristic mass spectrometric cracking pattern.

Although all aliphatic ketones photodissociate to some extent by free radical processes, evidence has accumulated that the more complex ketones having alkyl groups with γ-hydrogens also react to a significant degree by a concerted intramolecular rearrangement that gives an olefin and a lower ketone.[3,4] For example, it is now well established that methyl *n*-butyl ketone photodissociates to a large extent by this type of process into acetone and propylene.[5,6]

A major purpose of the present research was to irradiate methyl neopentyl ketone under a variety of conditions and determine the effect a large, highly branched, alkyl group with many primary γ-hydrogens might have on the efficiency of this rearrangement.

Experimental

Photolyses were carried out in a cylindrical quartz cell having an outside diameter of 3.0 cm. and a volume of 123 cc. The light source, a medium pressure mercury arc, Hanovia Type 73A, was operated at approximately 4.3 amp. and 145 v. A.C. It gave essentially constant intensities at both 2654 and 3130 Å. The lamp was mounted in a water-cooled housing attached directly to a Farrand Model 300 UV monochromator. A quartz lens, two inches in diameter with a six inch focal length, served to fill the reaction cell with collimated light.

Relative intensities were obtained by means of an RCA-935 phototube operated on a 180 volt battery power supply. The phototube current was measured with a No. 10-210 American Instrument Co. "Microphotometer." This instrument is designed primarily for use with a photomultiplier tube but was adapted for the 935 tube by connecting the anode of the 935 to pin 10 of the photomultiplier socket in the input lead of the "Microphotometer." A variable 5 megohm shunt in parallel with the "Microphotometer" was employed to extend the range of the instrument to large phototube currents. Acetone at 120° was used as an internal actinometer, with Φ_{CO} assumed to be unity at both 3130 and 2654 Å. The reaction cell was placed in an aluminum block furnace controlled by a Brown potentiometer. Methyl

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[1] From the Ph.D. Dissertation of T. W. Martin, Northwestern University, 1954. (b) Presented in part at the Conference on Photochemistry and Free Radicals, University of Rochester, September, 1954.

[2] Division of Physical Sciences, University of California, Riverside, California.

[3] A. J. C. Nicholson, *Trans. Faraday Soc.*, **50**, 1067 (1954).

[4] C. R. Masson, THIS JOURNAL, **74**, 4731 (1952).

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

[6] W. Davis, Jr., and W. A. Noyes, Jr., THIS JOURNAL, **69**, 2153 (1947).

neopentyl ketone has a vapor pressure of only 14 mm. at 25°, so it was necessary to use a heated inlet system and to enclose the entire reaction section, including cell, trap, manometer and inlet and exit stopcocks, within an air-thermostated transite box which could be heated to 100° and controlled to about ±1°. The concentration of methyl neopentyl ketone was kept essentially constant in all runs.

The methyl neopentyl ketone was prepared by the chromic acid oxidation of diisobutylene[7] as described by Seubold[8] and the crude material boiling between 122–125° was redistilled through a "50-plate" Podbielniak column at a reflux ratio of about 40:1. The fraction having a constant refractive index of $n^{25}\text{D}$ 1.4017 was distilled *in vacuo* into the ketone reservoir and stored over $CO_2(s)$. Mallinckrodt "Analytical Grade" acetone was stored over Drierite, then distilled *in vacuo* into the actinometer reservoir.

All photolyses were carried only to 1 or 2% decomposition. Two LeRoy stills[9] in series were used to separate the products into three fractions. The first still was set 5° warmer than the second; fraction A, collected at −155°, contained CO, methane and ethane with impurities of one per cent. or less of C_4 hydrocarbons; fraction B collected at −115°, contained isobutylene, isobutane and neopentane; and fraction C, collected at −78°, was largely acetone together with about 2% of the unreacted methyl neopentyl ketone and a smaller amount of diisobutylene. The latter compound seemed to be a small impurity carried over from the synthesis of methyl neopentyl ketone. No attempt was made to characterize products volatile above −78° because of the great difficulty in separating them from the very large excess of unreacted ketone. Fractions A and B were transferred into small glass thimbles by means of a Toepler pump and stored over mercury. After the volumes of each of these fractions had been measured with a Blacet–Leighton apparatus, the CO in A was determined with the use of either silver oxide pellets or fused cupric oxide–potassium hydroxide beads. Portions of A and B were then analyzed for each component with a Westinghouse Type LV mass spectrometer. Fraction C was collected directly in a freeze-out tube of known volume and kept at −195° until ready for analysis with the mass spectrometer. The mass spectrometer was calibrated frequently with the appropriate pure gases, with care being taken to use the same timing sequence of peaks as employed with the unknown samples. Pure samples of acetone, neopentane[10] and methyl neopentyl ketone could not be made up with the Blacet–Leighton apparatus, so they were prepared with the use of the calibrated freeze-out tube.

Experimental Results

The quantum yields of the products volatile at −78° from the photolysis of methyl neopentyl ketone are given in Tables I and II. In general, reasonable analytical precision was obtained for the hydrocarbons, but the carbon monoxide and acetone analyses were more scattered. Most of the acetone values are believed to be somewhat low, some by perhaps as much as 25%, because this product is difficult to recover from the very large excess of methyl neopentyl ketone and from the stopcock grease in the vacuum system. A dark run at 250° for 8 hr. resulted in no appreciable decomposition of methyl neopentyl ketone.

In order to test further the generality of intramolecular processes in the aliphatic ketones, one run was made on methyl isobutyl ketone under the same conditions as employed with the neopentyl compound. The results are shown in Table III. The value for acetone is low since no attempt was made to separate it quantitatively from the very large excess of methyl isobutyl ketone.

TABLE I

THE EFFECT OF TEMPERATURE ON QUANTUM YIELDS OF THE NON-CONDENSABLE PRODUCTS OF METHYL NEOPENTYL KETONE PHOTOLYSES AT 3130 Å.

Temp., °C.	120	120	170	210	250
Experiment	8	12	9	11	10
Pressure MNK, mm.	48	44	49	53	58
Pressure/temp., mm./°K.	0.122	0.112	0.111	0.110	0.111
Time, sec. $\times 10^{-4}$	2.88	2.88	2.88	2.88	2.88
Incident intensity, (quanta/cc. sec.) $\times 10^{-12}$	3.54	3.54	3.54	3.54	3.54
Fraction absorbed	0.557	0.570	0.578	0.620	0.642
Vol. CO, cu. mm., STP	.....	11.4	21.6	21.9	52.1
Quantum yields, Φ					
Isobutylene	0.23	0.23	0.24	0.28	0.27
Acetone	.18	[a]	.24	.25	[a]
Carbon monoxide	[a]	$.04_2$	$.07_9$	$.07_5$	.17
Methane	$.02_6$	$.02_2$	$.03_8$	$.04_8$	.13
Ethane	.005	.007	.008	$.01_3$	$.02_3$
Isobutane	.005	.006	.009	$.01_2$	$.02_0$
Neopentane	$.01_8$	$.02_0$	$.02_7$	$.03_0$	$.02_5$

[a] Not determined.

TABLE II

THE EFFECT OF TEMPERATURE ON QUANTUM YIELDS OF THE NON-CONDENSABLE PRODUCTS OF METHYL NEOPENTYL KETONE PHOTOLYSES AT 2654 Å.

Temp., °C.	120	170	170	210	250
Experiment	13	15	16	14	17
Pressure MNK, mm.	44	50	51	51	56
Pressure/temp., mm./°K.	0.112	0.113	0.115	0.105	0.107
Time, sec. $\times 10^{-4}$	2.88	2.88	2.88	2.88	2.88
Intensity (quanta/cc. sec.) $\times 10^{-12}$	2.88	2.88	2.88	2.88	2.88
Fraction absorbed	0.549	0.560	0.565	0.537	0.555
Vol. CO, cu. mm., STP	14.7	14.4	11.8	18.3	14.9
Quantum yields, Φ					
Isobutylene	0.24	0.29	0.32	0.30	0.39
Acetone	.20	.22	.31	.25	.33
Carbon monoxide	$.07_0$	$.06_7$	$.05_5$	$.09_0$	$.07_1$
Methane	$.02_9$	$.03_0$	$.03_7$	$.04_4$	.11
Ethane	$.01_4$	$.01_0$	$.00_9$	$.01_0$	$.01_4$
Isobutane	.005	.005	.005	.008	$.01_3$
Neopentane	$.02_1$	$.02_5$	$.02_7$	$.02_4$	$.02_0$

TABLE III

QUANTUM YIELDS OF THE NON-CONDENSABLE PRODUCTS OF THE PHOTOLYSIS OF METHYL ISOBUTYL KETONE AT 3130 Å. AND 120°

Pressure of ketone, mm.	49
Time, sec. $\times 10^{-4}$	2.88
Incident intensity, (quanta/cc. sec.) $\times 10^{-12}$	5.74
Fraction absorbed	0.535
Quantum yields	
Propylene	0.35
Acetone	0.09[a]
Carbon monoxide	0.15
Methane	0.09_7
Ethane	0.01_1
Isobutane	0.04_8
Isobutylene	0.006
Isopentane	0.014
Pentene	Trace

[a] Low. Not quantitatively separated.

Discussion

On the basis of this experimental evidence, and in light of the established work in ketone photochemistry, the following primary processes are proposed to explain the major aspects of the photolysis of methyl neopentyl ketone.

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(7) The diisobutylene was kindly supplied by the Shell Oil Co.

(8) F. H. Seubold, Jr., Ph.D. Thesis, University of California at Los Angeles (1947).

(9) D. J. LeRoy, *Canadian J. Research*, **B28**, 492 (1950).

(10) The pure neopentane was generously supplied by Professors R. L. Burwell, Jr., and H. Pines.

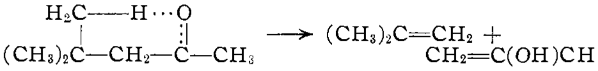
$$(CH_3)_3C\text{-}CH_2CO\text{-}CH_3 + h\nu \longrightarrow \begin{cases} (CH_3)_2C{=}CH_2 + CH_3COCH_3 & \text{(I)} \\ (CH_3)_3CCH_2 + CH_3CO & \text{(II)} \\ (CH_3)_3CCH_2CO + CH_3 & \text{(III)} \\ (CH_3)_3CCH_2 + CO + CH_3 & \text{(IV)} \\ (CH_3)_3C + CH_2COCH_3 & \text{(V)} \\ [(CH_3)_3CCH_2COCH_3]^* & \text{(VI)} \end{cases}$$

Primary Process (I).—Isobutylene and acetone are the major products from the photolysis of this ketone and it is proposed that they arise chiefly from I. The arguments in favor of this intramolecular process are the following.

(1) The ratio of the quantum yield of isobutylene to that of acetone is virtually constant and close to unity under all experimental conditions. On the average, the yield of isobutylene is about 15% greater than acetone, and it is felt this is primarily due to incomplete separation of the relatively small amounts of acetone from the large amounts of unreacted ketone. However, there is also some indication, particularly at 2654 Å. and 250°, that part of the excess isobutylene may arise from the decomposition of neopentyl radicals or other complex radicals, or from disproportionation of *t*-butyl radicals from V. Iodine inhibition studies could settle this point.

(2) The quantum yields of isobutylene and acetone are independent of temperature over a wide range at both 3130 and 2654 Å. This fact is good evidence that they both are formed in a primary photochemical process. The increase in $\Phi_{C_4H_8}$ at 2654 Å. and 250° seems to be real. The excess isobutylene may come from the secondary reactions indicated above.

(3) This process is analogous to that originally proposed by Norrish[5] and later developed by Davis and Noyes[6] to explain their detailed work on methyl *n*-butyl ketone. More recently Masson[4] and Nicholson[3] also have employed this type of intramolecular process to explain the photochemical behavior of certain aliphatic ketones having γ-hydrogen atoms, while Blacet and Calvert have demonstrated that *n*-butyraldehyde undergoes a similar photoreaction to give ethylene and acetaldehyde.[11] In the Davis and Noyes picture, reaction (I) can be visualized as taking place through the decomposition of a photoactivated six-membered cyclic configuration involving partial bonding to the oxygen atom by a γ-hydrogen atom. Cleavage of the α,β-carbon bond, accompanied by complete transfer of the γ-hydrogen atom, leads to isobutylene and enol acetone in one concerted step.



$$\begin{array}{l} H_2C\text{——}H\cdots O \\ (CH_3)_2C\text{—}CH_2\text{—}C\text{—}CH_3 \end{array} \longrightarrow \begin{array}{r} (CH_3)_2C{=}CH_2 + \\ CH_2{=}C(OH)CH \end{array}$$

However, an alternative picture also exists in which a γ-hydrogen atom might be directly transferred to the secondary α-carbon atom without the formation of an enol intermediate. To date there is little direct evidence as to which of these two detailed mechanisms, if either, is correct. However, it does now seem well established that only those ketones having γ-hydrogen atoms can participate effectively in this type of rearrangement.

It is apparent from the data in Table III that propylene is the major gaseous product in the photolysis of methyl isobutyl ketone. Acetone is also a product, and by analogy with methyl *n*-butyl and methyl neopentyl ketone it seems reasonable to assume that the olefin arises from an intramolecular process analogous to (I), namely

$$CH_3COCH_2CH(CH_3)_2 + h\nu \longrightarrow CH_3COCH_3 + CH_2{=}CHCH_3 \quad \text{(I')}$$

In the case of these methyl ketones it is interesting to compare, as in Table IV, the quantum efficiencies of olefin production by this intramolecular process, Φ_I, with the quantum yields of carbon monoxide from free radical processes, Φ_{CO}.

TABLE IV

QUANTUM YIELDS OF REARRANGEMENT, Φ_I, AND OF CO PRODUCTION FOR METHYL KETONES AT 3130 Å. AND 100–120°

Ketone	Φ_I	Φ_{CO}	Φ_I/Φ_{CO}	Reference
CH_3COCH_3	0.0	1.00	0.0	12
$CH_3COCH_2CH_3$	.0	0.84	0.0	13
$CH_3CO(CH_2)_3CH_3$	.48	.11	4.4	6
$CH_3COCH_2CH(CH_3)_2$	.35	.15	2.3	
$CH_3COCH_2C(CH_3)_3$	.23	.04	5.8	

The quantum yield of propylene from methyl *n*-butyl ketone substantially exceeds that for the isobutyl analog. This seems reasonable on the basis that the two secondary γ-hydrogen atoms more readily participate in the rearrangement than the six primary γ-hydrogens in the branched chain. Furthermore, although the absolute value of $\Phi_{C_3H_6}$ for methyl isobutyl ketone is greater than Φ isobutylene from the neopentyl ketone, the ratio Φ_I/Φ_{CO} is greater for the latter compound. This is in line with the greater number of γ-hydrogens on the more complex ketone.

Further support for the idea that a γ-hydrogen atom is necessary for this concerted process, comes from a recent study of Whiteway and Masson[14] who found that the photolysis of diisopropyl ketone proceeded entirely by free radical processes, with Φ_{CO} being unity from 50 to 150°. This is in contrast to the case of the di-*n*-propyl analog in which about 40% of the decomposition occurs by way of rearrangement to give ethylene and methyl *n*-propyl ketone.

An interesting correlation has been observed by these authors,[1b] and independently by Nicholson,[3] between the extent of this photochemical intramolecular process and the mass spectrometric cracking patterns of the higher aliphatic methyl ketones. The mass spectra of ketones which possess a γ-hydrogen atom and dissociate photochemically to give acetone and an olefin also show significant rearrangement peaks at *m/e* 58 which probably arise from acetone molecule–ions formed on electron impact. Furthermore, in the limited number of cases for which quantum yield and mass spectral data are both available, there seems to be a semiquantitative relationship between the quantum

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(11) P. E. Blacet and J. G. Calvert, THIS JOURNAL, **73**, 667 (1951).

(12) D. S. Herr and W. A. Noyes, Jr., *ibid.*, **62**, 2052 (1940).

(13) J. N. Pitts, Jr., Doctoral Dissertation, UCLA, 1949.

(14) S. G. Whiteway and C. R. Masson, THIS JOURNAL, **77**, 1508 (1955).

yield of the photo-induced rearrangement (based on olefin yields at 3130 Å. and 100–120°) and *m/e* 58/43 sensitivity ratio. The qualitative and semi-quantitative aspects of this correlation will be discussed in detail in a forthcoming paper.

Primary Processes II, III and IV.—These reactions are typical free radical dissociations of photoactivated ketones; they are necessary to account for the formation of the carbon monoxide and most of the hydrocarbon products. The small yields prevented accurate separations and analyses of these products but some qualitative observations seem in order.

At elevated temperatures the acyl radicals formed in II and III probably dissociate rapidly into carbon monoxide and methyl and neopentyl radicals. Thus, at the temperatures used in this research and barring any appreciable hot atom effects, II and III are substantially equivalent to IV.

If the photolyses were to be carried out at room temperature, it would seem, by analogy with the results for methyl ethyl ketone,[15] that process II in which the neopentyl is the departing group would be favored over III in which a methyl radical is split off.

Primary Process V.—No direct assessment can be made of the absolute yield of primary process V without iodine inhibition runs but it seems likely that this is a much more important mode of decomposition than is indicated by the low yield of isobutane.

The radical products from V are relatively stable and rather than abstracting hydrogen atoms they would tend to combine or disproportionate. Combination would lead to relatively non-volatile products which would be carried over and "lost" in the complex condensable fraction, whereas disproportionation of *t*-butyl radicals would give isobutylene and isobutane. Since disproportionation is favored by perhaps as much as 4:1 over combination,[16] this process accounts in part for the fact that isobutylene is in excess of the acetone yield in most runs.

The total decomposition of methyl neopentyl ketone (Φ_{total}), as estimated by the sum of Φ_{CO}, $\Phi_{\text{isobutylene}}$ and $\Phi_{\text{isobutane}}$, ranges from about 0.28 at 120° and 3130 Å. to 0.47 at 250° and 2654 Å. Thus, about 50–75% of the excited molecules do not decompose. Process VI therefore is required. Although collisional deactivation is certainly involved in decreasing the over-all decomposition yield, no pressure studies have been made to assess its importance. Neither can the possibility of a lowering of Φ_{total} by fluorescence be excluded. It is of interest that an over-all total quantum yield of decomposition of di-*n*-propyl ketone of about 0.5 was reported by Masson.[4] Since Φ_{total} is 1.00 for the diisopropyl ketone, Whiteway and Masson[14] suggest that the vibrational energy of the excited molecule may be dissipated in the cyclic structure involving a γ-hydrogen atom. A similar explanation may apply for methyl neopentyl ketone.

The increased yield of methane relative to carbon monoxide at 2654 Å. and 250° may indicate the occurrence of another primary process, VII, involving a β-methyl split.

$$CH_3COCH_2C(CH_3)_3 + h\nu \longrightarrow CH_3COCH_2C(CH_3)_2 + CH_3 \quad \text{(VII)}$$

However, in this research there is no direct evidence for VII, and discussion of it must await further work.

Secondary Radical Reactions.—The secondary radical processes are minor compared to the intramolecular rearrangement and the small yields of products prevent a detailed kinetic analysis of the data. However, qualitatively it seems apparent from the quantum yields of the non-condensable products and their temperature dependence that they result from the usual thermal radical reactions of abstraction, dissociation, combination and disproportionation.

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Riverside, Calif.

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[15] J. N. Pitts, Jr., and F. E. Blacet, This Journal, **72**, 2810 (1950).

[16] J. G. Calvert, private communication.