

Introduction of two methyl groups increases the "blocking" effect to a factor of 90 (for methyl β,β -dimethylacrylate) and of 75 (for β,β -dimethylacrylonitrile). Only two examples of such a "blocking" have been reported,⁸ namely, this in 1,1,4,4-tetramethylbutadiene which amounts to a factor of 75 and that in 9,9-dimethylfulvene reducing the reactivity by a factor of 72.

The examples of methyl β,β -dimethylacrylate and β,β -dimethylacrylonitrile serve to show that the addition of methyl radicals to hetero-atoms is negligible if any. Such an addition must be slower by a factor greater than 100 than the addition to a carbon center. The reluctance of methyl radical

to add to a hetero-atom was pointed out in previous publications from this Laboratory⁸ and it was attributed to the increasing repulsion due to the presence of a lone pair of electrons.

Methyl affinity of 1-cyanocyclopentene seems to be too high. At the same time one notices that the rate of hydrogen abstraction from this compound also appears to be unduly high. No explanation is offered to account for these observations.

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Structure and Reactivity in the Radiolysis of Ketones

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A series of six ketones has been subjected to radiolysis at 25° with 3 Mev. gamma rays from the van der Graaf accelerator of the Shell Development Company. The compounds were: methyl *n*-propyl, methyl *n*-butyl, methyl *n*-amyl, methyl cyclopropyl, dicyclopropyl and methyl propenyl ketones. Detailed product analysis has been carried out and *G*-values for the various products are reported. With methyl *n*-propyl, methyl *n*-butyl and methyl *n*-amyl ketones degradation into radicals and an intramolecular formation of acetone and olefin are the main processes. Thus for methyl *n*-propyl ketone $G(\text{CO}) = 0.38$, $G(\text{CH}_4) = 0.42$, $G(\text{C}_3\text{H}_8) = 0.36$, $G(\text{C}_2\text{H}_4) = 0.15$ and $G(\text{acetone}) = 0.13$. Methyl *n*-propyl ketone also gives rise to appreciable amounts of acetaldehyde ($G = 0.12$) and propylene ($G = 0.09$). With the cyclopropyl and unsaturated compound photorearrangement to an isomer is the main process, and there is little gaseous product. Dicyclopropyl ketone is particularly stable toward radiolysis. ($\Sigma G(\text{gaseous product}) = 0.36$ compared to 1.88 for methyl *n*-propyl ketone.)

Introduction

Radiolysis studies with acetone, methyl ethyl ketone and diethyl ketone have been undertaken by Ausloos and Paulson¹ who found that the formation of the major products could be explained on the basis of well known radical reactions. Experiments with scavengers indicated that most of the methyl radicals became thermalized before abstracting hydrogen. A few experiments with methyl *n*-propyl and methyl *n*-butyl ketones gave appreciably lower yields of carbon monoxide. Thus, they obtained values of 0.48 and 0.40, respectively, for $G(\text{CO})$ as compared with 0.74 for the lower ketones. This effect is analogous to well recognized results of photochemical studies; ketones having gamma hydrogen atoms give appreciably lower quantum yields of carbon monoxide than for example acetone or diethyl ketone.^{2,3} Recently the effect of added acetone on hydrogen formation in the radiolysis of 2-propanol has been investigated in detail,⁴ and it was concluded that acetone is an efficient trap for hydrogen atoms formed in the photolysis of this substance.

A more detailed examination of the radiolysis of ketones having gamma hydrogen atoms has been undertaken. In order to obtain a more comprehensive picture of the effects of molecular structure on the modes of decomposition by radiolysis, we have included an α,β -unsaturated ketone and two

ketones containing cyclopropyl groups. The gas phase photochemistry of these substances has already been investigated in these laboratories.⁵⁻⁷

Experimental

The six ketones were purified by preparative GL-Chromatography using the Beckman Megachrom with a silicone oil stationary phase. This instrument will handle 20 ml. samples, which makes it possible to prepare appreciable quantities of material of high purity. The purified compounds were chromatographed on a conventional column with a Ucon Polar stationary phase to check their purity and to provide reference chromatograms for comparison with the irradiated material. Dicyclopropyl ketone still showed an impurity of 2-3% which is not resolved from dicyclopropyl ketone by a silicone column. The other ketones had a total impurity of less than 1/2%.

Two one ml. samples of each compound were weighed and distilled under vacuum into 10 mm. diameter sample tubes having a glass break-off seal. In addition, two samples each of methyl *n*-propyl, methyl *n*-butyl and methyl *n*-amyl ketones were prepared and iodine added to a concentration of approximately $5 \times 10^{-3} M$. Three of these samples with iodine were kept as blanks (one of each ketone), and the rest of the samples were shipped to the Shell Development Company at Emeryville, California, for irradiation with 3Mev. van der Graaf Bremsstrahlung. Each tube was irradiated for 15 minutes at 25° at a dose rate of 1.46×10^8 rads./hour (1 rad. = 100 ergs/g.).

Primary separation of products for analysis was carried out under vacuum using a solid nitrogen trap, a LeRoy-Ward still, a mercury diffusion pump and a Toepler pump with calibrated gas buret. In each case the break-off seal was broken with a glass enclosed piece of iron, which could be manipulated with a magnet external to the apparatus. The sample was immersed in a bath of Dry Ice

(1) P. Ausloos and J. F. Paulson, *J. Am. Chem. Soc.*, **80**, 5117 (1954).

(2) W. Davis, Jr., and W. A. Noyes, Jr., *ibid.*, **69**, 2153 (1947).

(3) For a review see J. N. Pitts, Jr., *J. Chem. Educ.*, **34**, 112 (1957).

(4) J. D. Strong and J. G. Burr, *J. Am. Chem. Soc.*, **81**, 775 (1959).

(5) R. S. Tolberg and J. N. Pitts, Jr., *ibid.*, **80**, 1304 (1958).

(6) J. N. Pitts, Jr., and I. Norman, *ibid.*, **76**, 4815 (1954).

(7) J. N. Pitts, Jr., and R. S. Woolfolk, Abstracts, 133rd Meeting Am. Chem. Soc., April 1958, p. 4-Q.

and products volatile at -215° were pumped into the gas buret and measured. A thermocouple gage indicated when all the product volatile at -215° had been removed. This cut comprising hydrogen, methane and carbon monoxide was transferred to a small storage bulb standing over mercury for mass spectral analysis. For the second cut, the solid nitrogen trap was removed and the fraction volatile at -115° was taken from the Ward Still. This fraction was similarly measured and stored for mass spectral analysis. Finally the Ward still was allowed to warm to room temperature and the remaining products were distilled back into the original sample tube for liquid product analysis.

Liquid products were chromatographed on an Aerograph under the same conditions as those used in obtaining the reference chromatograms. Individual products were trapped at the exit to the chromatography unit in a small U-tube made of 3 mm. Pyrex. The amount of product trapped during any one experiment was of the order of $1/8$ μ mole. These compounds were introduced to the mass spectrometer or infrared or ultraviolet spectrophotometer for identification analysis. Calculations of absolute amounts of product were made using the areas under the chromatogram peaks. The instrument was calibrated with pure substances in most cases. In those cases where the pure substance was not available, its sensitivity was inferred from the sensitivities of related substances. For infrared analysis the product was collected and taken up in 10 μ l. of carbon tetrachloride. The solution was introduced to a 0.1 mm. capillary cell and analysed with a Perkin Elmer Model 221-G.

Results and Discussion

(a) **Saturated Ketones.**—Product yields for methyl *n*-propyl, methyl *n*-butyl and methyl *n*-amyl ketones are given in Table I. Yields are listed as *G*-values which are the number of molecules of product formed per 100 electron volts of radiant energy.

TABLE I
G VALUES FOR PRODUCTS OF THE RADIOLYSIS OF METHYL *n*-PROPYL, METHYL *n*-BUTYL AND METHYL *n*-AMYL KETONES

	Methyl <i>n</i> -propyl ketone	Methyl <i>n</i> -butyl ketone	Methyl <i>n</i> -amyl ketone
Hydrogen	0.45	0.57	1.14
Methane	.42	.29	0.26
Carbon monoxide	.38	.29	.22
Ethylene	.15	.039	.090
Ethane	.026	.059	.032
Propylene	.092	.29	...
Propane	.36	.11	...
Butene-116
Butane20	.02
Pentane32
Acetone	.13	.36	.40
Acetaldehyde	.12
Methyl <i>n</i> -propyl ketone026	.032
Methyl <i>n</i> -butyl ketone058

Hydrogen, methane and carbon monoxide are major products in each case. $G(\text{H}_2)$ increased from 0.45 for methyl *n*-propyl to 1.14 for methyl *n*-amyl ketone. This probably is due, at least in part, to the fact that there are more secondary hydrogen atoms present as the homologous series is ascended, and these are relatively more susceptible to gamma radiation.⁸ $G(\text{CH}_4)$ and $G(\text{CO})$ decreased from propyl (0.42 and 0.38) to amyl (0.26 and 0.22, respectively) and were much lower than the values obtained by Ausloos and Paulson¹ for acetone and diethyl ketone. For example, these

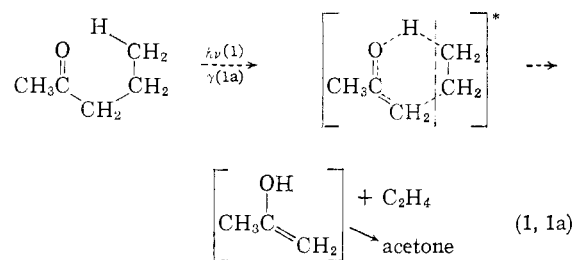
(8) J. G. Burr, *J. Phys. Chem.*, **61**, 1477 (1957).

authors obtained $G(\text{CH}_4) = 2.6$ and $G(\text{CO}) = 0.8$ for acetone at 27° .

It can be seen from our results that acetone and, respectively, ethylene, propylene and butene-1 were major products for methyl *n*-propyl, methyl *n*-butyl and methyl *n*-amyl ketones. In the last case the identity of the butene was established by vapor-phase chromatography using a 30 ft. column of 2,5-hexanedione at room temperature. No other butenes were observed. This confirms the qualitative observations of Ausloos and Paulson¹ for methyl *n*-propyl and methyl *n*-butyl ketones. $G(\text{acetone})$ and $G(\text{olefin})$ are comparable except for methyl *n*-amyl ketone. In this case the low value of $G(\text{C}_4\text{H}_8)$ probably is due to failure to separate all of the butene-1 at -115° from the radiolyzed ketone.

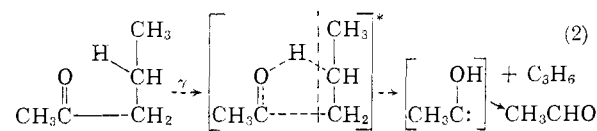
These results can be explained on the basis of a gamma ray initiated rearrangement (1a) analogous to the well known photochemical intramolecular process 1 for ketones with gamma hydrogens (the Norrish Type II process).

There is strong evidence that this process occurs by way of a cyclic intermediate in which a gamma hydrogen atom is in close proximity to the carbonyl oxygen.^{2,9-12} The intermediate decomposes to give an olefin and enol acetone.



The same intermediate may be involved in both radiolysis and photolysis systems. Certainly, the equivalence of *G* values for acetone and olefin strongly support an intramolecular process.

A similar process may account for the formation of acetaldehyde and propylene in the radiolysis of methyl *n*-propyl ketone.



(In this case presumably a beta hydrogen might be transferred to the carbonyl oxygen.)

For methyl *n*-propyl ketone reaction 2 might be favored because it involves a secondary hydrogen atom, whereas (1a) requires reaction of a primary hydrogen atom. Presumably with methyl *n*-butyl and *n*-amyl ketones acetaldehyde would not be formed because in these cases the gamma hydrogen atoms are also secondary and everything would be in favor of reaction 1.

(9) A. J. C. Nicholson, *Trans. Faraday Soc.*, **50**, 1067 (1954).

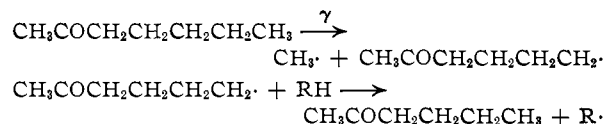
(10) R. Srinivasan, *J. Am. Chem. Soc.*, **81**, 5061 (1959).

(11) P. Ausloos, Abstracts, 138th Meeting Am. Chem. Soc., Sept. 1960, p. 5-S.

(12) W. Brunet and W. A. Noyes, Jr., *Bull. Soc. Chim. France*, **121** (1958).

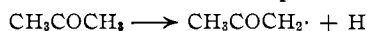
It is interesting that $G(\text{acetone})$ was much higher for the n -butyl and n -amyl ketones than for n -propyl [0.13 compared to 0.36 and 0.40, respectively]. However, if one takes $G(\text{acetone}) + G(\text{acetaldehyde})$ as a measure of the extent of intramolecular rearrangement then $G(\text{intramol. rearr.}) = 0.27, 0.36$ and 0.40 , respectively, which is a more consistent trend than that given by $G(\text{acetone})$ alone.

Methyl n -butyl and methyl n -amyl ketones also gave smaller yields of lower homologs. These probably arise from minor radical reactions, *e.g.*



There is insufficient information to warrant detailed discussion of a mechanism for the formation of these substances.

Three samples containing $10^{-3} M$ iodine yielded G values which were essentially the same as those in absence of iodine. Ausloos and Paulson¹ found for acetone, methyl ethyl ketone and diethyl ketone, that $G(\text{CH}_4)$ and $G(\text{C}_2\text{H}_6)$ were appreciably reduced (85%) when $10^{-2} M$ iodine was present but that $G(\text{H}_2)$ and $G(\text{CO})$ were reduced only approximately 25%. This is accounted for by assuming that H atoms formed in a process such as



carry over a large excess of kinetic energy and abstract hydrogen before they ever meet a scavenger molecule, whereas methyl radicals largely become thermalized and form methane by a normal abstraction process. $G(\text{CH}_4)$ would then be appreciably decreased in the presence of scavenger. In our case the lack of dependence of the yields on the presence or absence of iodine may be because there is a critical iodine concentration above which iodine is effective which was not reached in our case—we used $10^{-3} M$ iodine (*cf.* Ausloos $10^{-2} M$), or it may be that in our case "hotter" radicals were produced; Ausloos and Paulson used Co^{60} gamma radiation which is 1.17 and 1.33 Mev.

(b) **Cyclopropyl and α,β -Unsaturated Ketones.**—These ketones gave comparatively little gaseous product as can be seen from Table II which shows ΣG -gaseous product for each of the six ketones.

TABLE II

ΣG -GASEOUS PRODUCT IN LIQUID PHASE RADIOLYSIS AT 25°

Methyl n -propyl	Methyl n -butyl	Methyl n -amyl	Methyl propenyl	Methyl cyclopropyl	Di-cyclopropyl
1.88	1.85	2.24	0.52	0.62	0.36

This is analogous to the photochemical behavior of these substances. Thus, *trans*-methyl propenyl ketone has been studied by Tolberg and Pitts, who found that this compound is remarkably stable toward photodecomposition even at 275°. The only significant reaction was a photoisomerization to the *cis* form. Similarly methyl cyclopropyl ketone⁶ and dicyclopropyl⁷ gave only small yields of carbon monoxide, methane and C_3 hydrocarbons under photolysis. In these cases photoisomeriza-

tion of cyclopropyl to propenyl groups was the only important process.

Table III shows the G values for these ketones. Dicyclopropyl ketone was exceptionally stable toward radiolysis. Hydrogen and ethylene were the main products with smaller amounts of carbon monoxide, cyclopropane, acetylene and propyne. The stability of dicyclopropyl ketone must be put down to the presence of small ring substituents in the molecule.

TABLE III

G VALUES FOR THE PRODUCTS OF THE RADIOLYSIS OF METHYL CYCLOPROPYL, DICYCLOPROPYL AND METHYL PROPENYL KETONES

	Methyl cyclopropyl ketone	Dicyclopropyl ketone	Methyl propenyl ketone
Hydrogen	0.18	0.13	0.25
Methane	.17	.011	.066
Carbon monoxide	.17	.030	.14
Ethylene	.056	.088	...
Ethane	.006005
Propylene	.012	.041	.007
Butene-1	.003003
Acetylene	.006	.014	.005
Propyne	.003	.019	...
Cyclopropane	.006	.028	...
Methyl isopropenyl ketone50
<i>cis</i> -Methyl propenyl ketone15
Propenyl substituted ketone	.007	.014	...
Propyl substituted ketone	.014	.023	...

Methyl cyclopropyl ketone was intermediate in stability between dicyclopropyl ketone and the aliphatic ketones. This compound gave hydrogen, carbon monoxide and methane but only traces of hydrocarbon as products. These substances each showed small amounts of two liquid products on the chromatogram. From their retention times and mass and infrared spectra we believe, in the case of methyl cyclopropyl ketone, that these are methyl n -propyl and methyl propenyl ketones. Unambiguous identification was rendered impossible by the small yield. The former compound had large mass spectral peaks at m/e 43 and 71 with small peaks at m/e 86 and 58. The m/e 58 peak distinguishes the n -propyl from the isopropyl ketone. The second compound had peaks at m/e 41, 43, 69 and 84 and showed evidence of conjugation by a shift in the infrared carbonyl band toward the red.

Similarly, from their mass and infrared spectra and by analogy with methyl cyclopropyl ketone, we believe the two products from dicyclopropyl ketone radiolysis to be ketones with propyl and propenyl substituents.

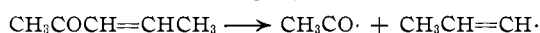
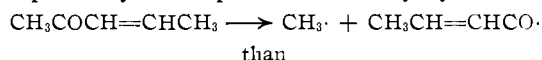
trans-Methyl propenyl ketone ($\text{CH}_3\text{COCH}=\text{CHCH}_3$) isomerized on irradiation to the *cis*-methyl propenyl and isopropenyl ketones. *trans-cis* Photoconversions are common.¹³ For ex-

(13) "Techniques of Organic Chemistry," Vol. II, p. 336, Interscience Publishers, Inc., New York, N. Y.

ample, vapor phase photolysis of *trans*-methyl propenyl ketone yields the *cis* isomer.⁵

The formation of methyl isopropenyl ketone [CH₃COC(CH₃)CH₂] require migration of a methyl group and a hydrogen atom and probably occurs by a decomposition-recombination process.

Yields of methane and propylene (0.07 and 0.01) are low but *G*(CH₄) is appreciably higher than *G*(C₃H₆). Excited methyl propenyl ketone molecules probably decompose more readily by



because the crotonyl radical (CH₃CH=CHCO·) is resonance stabilized. These radicals once formed do not decompose readily to give CO and CH₃-CH=CH.¹⁴

It is evident that unsaturated and cyclo substituted ketones are much more stable toward decomposition into radicals under radiolysis than saturated ketones and thus analogous with their photolytic behavior. The stability of unsaturated ketones may be put down in part to stability imparted by conjugation. However, non-conjugated ketones are also stable toward decomposition into radicals. Thus, Srinivasan¹⁵ found that 5-hexene-

(14) A. D. Osborne and G. Skirrow, *J. Chem. Soc.*, 2750 (1960).

(15) R. Srinivasan, *J. Am. Chem. Soc.*, **82**, 775 (1960).

2-one was remarkably stable toward photodecomposition and experiments in these laboratories confirm this observation.

By analogy one would expect methyl allyl ketone to be stable toward radiolysis. We have obtained radiolysis data on this compound which indicate that such is the case. However, we had reservations concerning the purity of our sample, and it was felt that the results did not warrant inclusion and discussion with the other data.

Acknowledgments.—Certain preliminary experiments in this investigation were conducted by Mr. J. Swinehart, whom we wish to thank. This research was supported in part by grants to J.N.P. from the Petroleum Research Fund of the American Chemical Society, Grant No. PRF 278-A, and the U. S. Public Health Service through Grant RG-7005. We are deeply indebted to these granting agencies and to Drs. D. P. Stevenson, Robert Brattain and John Otvos of the Shell Development Company at Emeryville, California, who made available their facilities, and to Dr. Charles Wagner and Mr. E. R. Bell, who directed the laboratory radiolyses and provided us with many stimulating discussions on radiation chemistry. J.N.P. also acknowledges with thanks his period as visiting scientist at the Shell Development Company, during which he initiated this research.

[CONTRIBUTION FROM THE RADIATION RESEARCH LABORATORIES, MELLON INSTITUTE, PITTSBURGH, PA.]

Photolysis of Phosgene in the Presence of Ethylene¹

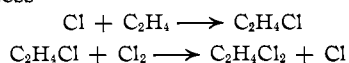
BY M. H. J. WIJNEN

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The photolysis of phosgene in the presence of ethylene has been carried out at various phosgene to ethylene ratios, and at different light intensities and temperatures. The results are quite different from those obtained by photochlorination of ethylene in the presence of molecular chlorine. The main reaction products were: carbon monoxide, 1-chlorobutane and 1,4-dichlorobutane. The formation of 1,4-dichlorobutane and 1-chlorobutane may be represented by the several reactions: 2C₂H₄Cl → (C₂H₄Cl)₂ (4); C₂H₄Cl + C₂H₄ → C₄H₈Cl (7); C₄H₈Cl + R → C₄H₉Cl + R'H (9). An activation energy of about 7.5 kcal. is proposed for reaction 7. The carbon monoxide yield is directly proportional to the absorbed light intensity and may be used as an internal standard for the amount of chlorine atoms produced.

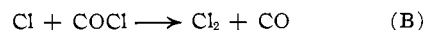
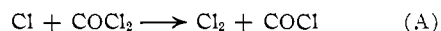
Introduction

The photochlorination of ethylene in the presence of molecular chlorine proceeds *via* the well-known chain process



The following information indicated that substitution of phosgene for molecular chlorine as the chlorine atom donor might prevent the occurrence of a chain reaction.

Schwab,² investigating the reactions of Cl atoms produced by the discharge tube method, observed that the addition of phosgene had very little effect on the chlorine atom concentration. Since consumption of Cl atoms would be expected by the sequence



he concluded that the activation energy of reaction A must be relatively high.

Bodenstein, Brenschede and Schumacher³ reviewed the work on reactions A and B in detail and concluded that *E*_A = 23 kcal.

Runge⁴ studied the photochemical reactions of oxalyl chloride and of phosgene with hydrocarbons. Chlorine atoms reacted with hydrocarbons to form HCl and alkyl radicals. No reaction was observed between alkyl radicals and phosgene.

These data indicate clearly that in the photolysis of phosgene no regeneration of chlorine atoms occurs by secondary reactions. The resulting reaction mechanism should thus be quite different from photochlorination processes in the presence of molecular chlorine.

(1) This work was supported in part by the U. S. Atomic Energy Commission.

(2) G. M. Schwab, *Z. physik. Chem.*, **A178**, 123 (1936).

(3) M. Bodenstein, W. Brenschede and H. J. Schumacher, *ibid.*, **B40**, 121 (1938).

(4) F. Runge, *Z. Elektrochem.*, **60**, 956 (1956).