Synthesis of Several Ketones from Acetaldehyde and Propylene by Gamma-ray Irradiation[*]

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It has been reported[1] mostly in the patent literature that some ketones are synthetized by a chain mechanism from aldehydes and terminal olefins at 60∼100°C, using benzoyl peroxide, acetyl peroxide etc. as initiator. The reaction is believed to involve the sequence,

$$RCHO \rightarrow R\dot{C}O + H$$

$$R\dot{C}O + CH_2{=}CHR' \rightarrow RCOCH_2\dot{C}HR'$$

$$RCOCH_2\dot{C}HR' + RCHO \rightarrow RCOCH_2CH_2R' + R\dot{C}O$$

A similar reaction has been initiated photochemically at room temperature. However, the reaction ought to proceed more easily by use of gamma-ray irradiation without any chemical initiator, because of its powerful action of producing free radicals. Such being the situation, it is interesting to investigate the above expectation in the system of acetaldehyde and propylene, because the yield of ketones was low when a chemical initiator was used[2]. It is the purpose of the present paper to report the result actually carried out.

Experimental

Materials.—*Acetaldehyde* was prepared by heating commercial paraaldehyde at 70°C, which had been purified by distillation, with a small amount of concentrated sulfuric acid. The final product was purified by repeating vacuum distillation twice. *Propylene* was prepared by dehydrating the middle fraction of the distillate of commercial isopropyl alcohol on alumina kept at 400°C. Impurities of the samples were found to be within 0.5% with mass-spectrometry and gas-chromatography.

Procedure. — All the samples were carefully deaerated by evacuation, then keeping them at

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[*] Preliminary report: the 3rd Isotope Symposium of Japan, R. 31, Tokyo, Sept. 15, 1959.

[1] Cf. C. Walling, "Free Radicals in Solution", John Wiley & Sons, New York (1957), p. 273.

[2] F. C. Ladd, U. S. Pat., 2,517, 684 (Aug. 8, 1950).

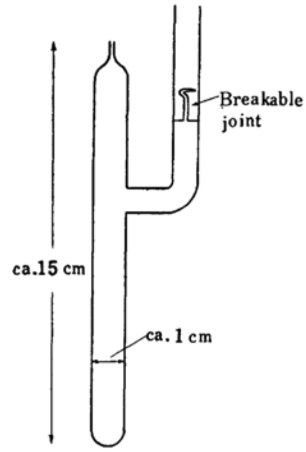


Fig. 1. Irradiation tube.

−190°C, enclosed and irradiated in the glass tube shown in Fig. 1. *Irradiation* was carried out on the samples enclosed in the tube with the Co-60 source (1000 curie) installed at Osaka Laboratory of JARRP. The dose rate was measured with the Fricke dosimeter. After irradiation, products were taken out from the tube by use of a breakable joint and were put to analysis.

Analysis.—After the amount of gaseous products was determined with the Saunder-Taylor apparatus, they were analyzed quantitatively by the mass-spectrometric method (apparatus: Hitachi RMU-5). Liquid products were analyzed by the gas-chromatographic method (apparatus: Shimadzu GClA; carrier gas: helium). Final identification of each product was made, however, by resorting to mass-spectrometry and infrared spectrometry on the samples fractionated by the gas-chromatograph except in the case of the higher boiling products, the chemical structure of which was estimated from their retention time.

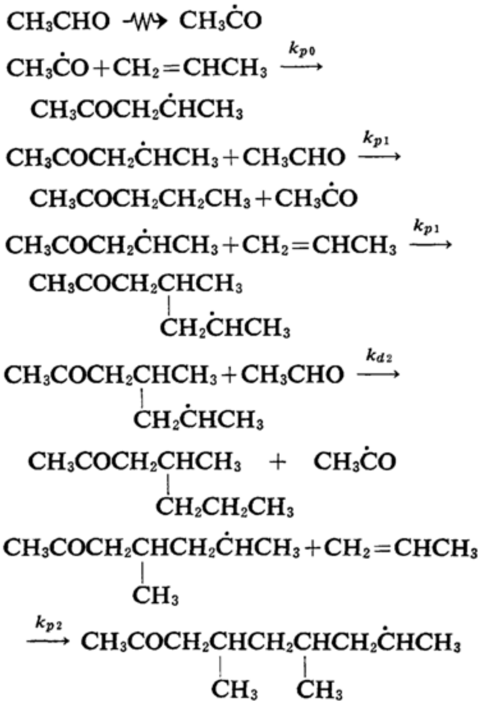
Results and Discussion

The gaseous products were hydrogen, methane and carbon monoxide, their *G* values being small as shown in Table I. From the liquid products, methylpropylketone (MPK), methylhexylketone (MHK), and methylnonylketone (MNK) could be identified by the gas-chromatographic method, using a high vacuum-oil-column (length 2.45 m.) at 180°C. The peak of MPK separated into two parts when the column charged with dioctyl phthalate was used. The peak which was larger in area by several times was found to be normal MPK (M*n*PK), while the other was its isomer, i. e., methylisopropylketone (M*i*PK). It is noteworthy that MPK's, MHK and MNK correspond to the ketones produced by the addition of one, two and three molecules of propylene to an acetaldehyde molecule, respectively.

TABLE I. EXAMPLES OF THE EXPERIMENT
Amounts of products are expressed in mol. × 10^{-4}; numbers in parentheses are *G* values.

	Experiment	1	2	3
	Acetaldehyde (mol.)	0.053	0.053	0.116
	Propylene (mol.)	0.05	0.031	0.032
	R=acetaldehyde/ propylene	1.0_4	1.7_1	3.6_2
	Total dose (r)	7×10^7	1×10^7	2×10^7
	Dose rate (r/hr.)	12.2×10^4	1.9×10^4	1.4×10^4
Products	Hydrogen	2.24(0.64)	0.5 (1.4)	—
	Carbon monoxide	1.16(0.35)	0.38(1.0)	—
	Methane	0.17(0.05)	0.11(0.2)	—
	MPK M*i*PK	6.0 (1.8)	2.8 (7.0)	8.7(5.7)
	MPK M*n*PK	29.0 (9.0)	2.4 (68)	128 (83)
	MHK	20 (6.0)	19.5 (60)	39 (28)
	MNK	6.0 (1.8)	4.3 (1.4)	5.0(3.3)

Considering that aldehyde is more sensitive to radiation than propylene and also that irradiation is carried out at room temperature, these ketones may be produced via acetyl radical by the following scheme:



$$\mathrm{CH_3CHO \rightsquigarrow CH_3\dot{C}O}$$

$$\mathrm{CH_3\dot{C}O + CH_2{=}CHCH_3 \xrightarrow{k_{p0}} CH_3COCH_2\dot{C}HCH_3}$$

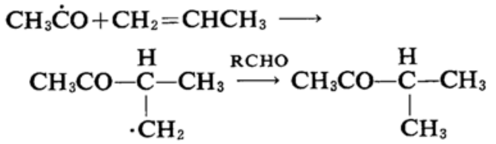
$$\mathrm{CH_3COCH_2\dot{C}HCH_3 + CH_3CHO \xrightarrow{k_{p1}} CH_3COCH_2CH_2CH_3 + CH_3\dot{C}O}$$

$$\mathrm{CH_3COCH_2\dot{C}HCH_3 + CH_2{=}CHCH_3 \xrightarrow{k_{p1}} CH_3COCH_2\underset{\displaystyle CH_2\dot{C}HCH_3}{\underset{|}{C}}HCH_3}$$

$$\mathrm{CH_3COCH_2\underset{\displaystyle CH_2\dot{C}HCH_3}{\underset{|}{C}}HCH_3 + CH_3CHO \xrightarrow{k_{d2}} CH_3COCH_2\underset{\displaystyle CH_2CH_2CH_3}{\underset{|}{C}}HCH_3 \ + \ CH_3\dot{C}O}$$

$$\mathrm{CH_3COCH_2\underset{\displaystyle CH_3}{\underset{|}{C}}HCH_2\dot{C}HCH_3 + CH_2{=}CHCH_3 \xrightarrow{k_{p2}} CH_3COCH_2\underset{\displaystyle CH_3}{\underset{|}{C}}HCH_2\underset{\displaystyle CH_3}{\underset{|}{C}}HCH_2\dot{C}HCH_3}$$

The above scheme coincides with the result that the *G* values of the produced ketones are higher than that of usual radiation-induced reaction. The produced ketones may therefore be expressed generally by $\mathrm{RCO(C_{3n}H_{6n+1})}$, thus M*n*PK, MHK and MNK being the ketones, *n* of which corresponds to 1, 2 and 3, respectively. However, the presence of a small amount of M*i*PK indicates a process slightly different from the above; i. e. the addition of acetyl radical to β-carbon of propylene as follows:



$$CH_3\dot{C}O+CH_2{=}CHCH_3 \longrightarrow CH_3CO{-}\underset{\cdot CH_2}{\overset{H}{C}}{-}CH_3 \xrightarrow{RCHO} CH_3CO{-}\underset{CH_3}{\overset{H}{C}}{-}CH_3$$

According to the mechanism, higher homologues of the ketone (n=4, 5, 6……) must be produced besides, even though in smaller amount. Actually they could not be identified in the residues of vacuum-distillation of the product, but their existence can be estimated by the following reasoning. In Fig. 2, molar fractions F_n of each ketone produced by the ratio 1 : n are plotted against aldehyde/propylene (R) as the abscissa, making the total dose and dose rate constant, i. e., at 2.3×10^7 r and 4.7×10^4 r/hr. respectively. The full line denotes the theoretical one[3], calculated by the formula,

$$F_n=\frac{C_nR}{\prod\limits_{i=1}^{n}(C_iR+1)} \tag{3}$$

where C_n's are transfer constants, k_{dn}/k_{pn}. When the following values were adopted, in actual calculation, $C_1=0.84$, $C_2=1.64$ and $C_3=6.1$, good coincidence between theoretical and observed data is obtained. Considering this result, even C_4 must be so large that homologues of ketone higher than MNK can be neglected practically, even though they are produced. Actually, if C_4 is assumed to be 20 and F_4 is calculated, it is very small as shown by the dotted line in Fig. 2.

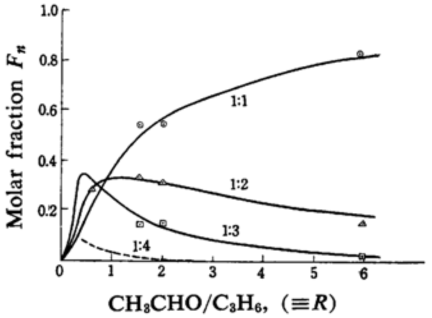


Fig. 2. Molar fraction of produced ketones vs. R*.
Dose rate, 4.7×10^4 r/hr.
Total dose, 2.3×10^7 r.
— Theoretical curves calculated by Eq. 3.

The terminating processes which follow the above propagating processes in the chain reaction must be ascribed to some recombination processes between radicals, e. g.

$$2CH_3\dot{C}O \longrightarrow (CH_3CO)_2$$

$$\text{or}\quad CH_3\dot{C}O+CH_3CO(C_3H_6)_nCH_2\dot{C}HCH_3 \longrightarrow CH_3CO(C_3H_6)_{n+1}COCH_3$$

Such processes may be reasonable if the fact that the yields of the ketones decrease with increasing dose rate as shown later is taken into account. However the products resulting from the recombination process could not be detected, probably because of their lower yields and of their larger retention time in the gas-chromatogram.

As shown in Fig. 3, where dose rate and total dose were kept constant at 4.7×10^4 r/hr. and 2.3×10^7 r., respectively, the amount of hydrogen was practically constant, while those of methane and carbon monoxide increased; this tendency is concordant with the expectation that the decomposition products of acetaldehyde increase with R.

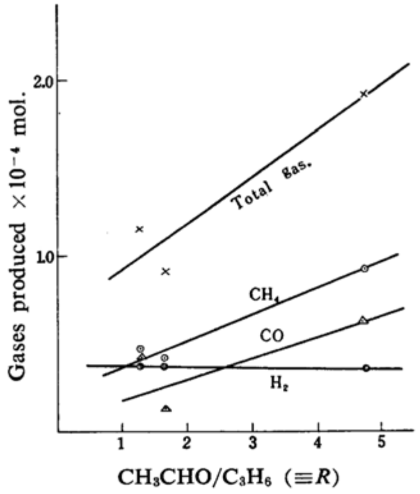


Fig. 3. Gases produced vs. R (molar ratio of acetaldehyde and propylene in the feed).
Total dose, 2.3×10^7 r.
Dose rate, 4.7×10^4 r/hr.

The effect of total dose on the ketones produced is shown in Fig. 4 where the dose rate and R were kept constant at 15.6×10^4 r/hr. and 1.6, respectively. It was found that the amounts of MPK, MHK and MNK increased with the total dose, but not linearly in the cases of MHK and MNK. This result may be explained by the fact the reaction order of propylene was greater than that of aldehyde in the cases of MHK and MNK, considering that the amount of the unreacted

* In Fig. 2∼5, 1 : n means the ketone produced by one mole of aldehyde and n moles of propylene.

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[3] Cf. p. 245 of Ref. 1.

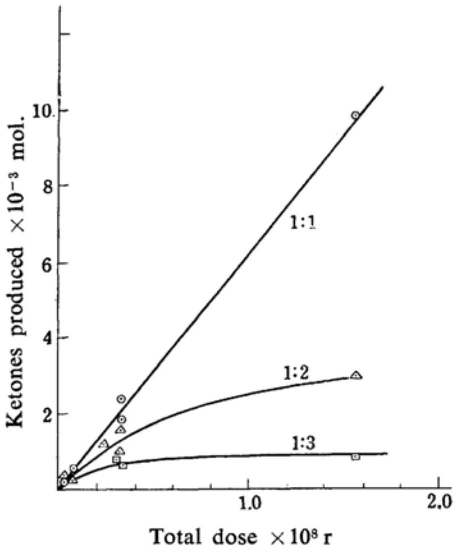

Fig. 4. Ketones produced vs. total dose. $R=1.6$, dose rate, 15.6×10^4 r/hr.

propylene was very small in the case of the highest total dose. The gases produced increased practically linearly against the total dose, but the amounts of hydrogen and methane were the same in the order of magnitude, while the amount of carbon monoxide was much smaller. Of course the order of their magnitude varied according to R as shown in Fig. 3.

In Fig. 5, the logarithm of the amounts of liquid products is plotted against the logarithm of the dose rate where the total dose and R were kept 2.3×10^7 r and 1.6, respectively. As compared with the liquid products, the amounts of the gaseous products were practically not affected by the dose rate, though the amounts of hydrogen and carbon monoxide decreased slightly while that of methane increase. The amounts of ketones decreased markedly against the dose rate, but a linear relation does not exist in Fig. 5. Such a result ought not to be obtained if the bimolecular termination of $CH_3\dot{C}O$ be realized as was done in the above reaction sceeme. However, since the data are still insufficient to derive any conclusion in regard to the mechanism, i. e., the number of measurements was small, and concentration of propylene was not constant during the reaction in some of the measurements, a definite conclusion on the effect of dose rate will be postponed to later research.

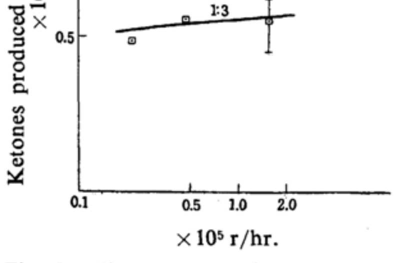

Fig. 5. The amounts of ketones produced vs. irradiation dose rate. $R=1.6$, total dose 2.3×10^7 r.

Finally we will see what can be said about this reaction if it is considered as a synthetic method. First, it is favorable for this method that the total yield of the produced ketones was larger than that of the method by which some chemical initiator is used. For instance in No. 3 in Table I, conversion of propylene into MPK, MHK and MNK amounted to 72%, the sum of their G values being 120. Second, G values will be increased markedly, if the temperature of the system is raised as much as possible. This expectation has been confirmed to some degree in the system of acetaldehyde and isobutylene4). However, it is interesting hereafter to determine the upper limit of the reaction temperature, considering that acetyl radical inclines to decompose into CH_3 and CO according to the degree of the temperature.

Summary

It has been found that methylpropylketone and other higher ketones are synthetized with relatively high G values by gamma-ray irradiation on mixtures of acetadehyde and propylene at room temperature, and that the reaction proceeds by a chain mechanism, with acetyl radical produced thereby as the initiator.

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4) K. Hirota, S. Iizuka and M. Hatada, *Abstracts of the 13th Annual Meeting of Chemical Society of Japan*, 49 (1960).