Columns used for the gas chromatographic analysis, depending on the requirements of the particular reaction mixture, were the following: a 7-foot, 1/4-inch column packed with 15% Silicone 550 (Dow Corning Corp.) on Chromosorb W; a 12-foot, 1/4-inch column packed with 12% Kel-F Grease (Minnesota Mining and Manufacturing Co.) on Chromosorb W; and a 10-foot, 1/4-inch column packed with 15% Oronite No. 16 (Oronite Chemical Co.) on Chromosorb W. The column temperature in each case was 78° with helium used as the carrier gas (helium head pressure, 10 p.s.i.g.). The samples were introduced unto the column with a 0.010 ml. pipette through a Fisher sample injection valve.

*Experimental procedure.* About 2 ml. of the olefin and 0.5 ml. of bromotrichloromethane were pipetted into the reaction tube. A 0.010-ml. sample of this mixture was analysed by gas chromatography and the area of the bromotrichloromethane peak measured with a planar compensating planimeter. The tube was sealed and placed in the constant temperature bath and allowed to reach thermal equilibrium. The tube and its contents were then illuminated by the sun lamp, which was placed about 15 to 20 in. from the bath to exclude any external heating from the lamp, for a period of 5–20 min. in order to allow about 50–75% of the bromotrichloromethane to react. The tube was removed from the bath and allowed to reach room temperature and a 0.010-ml. sample was analysed by gas chromatography under conditions identical to those employed for the first sample. The areas of the bromotrichloromethane and chloroform were determined with a planimeter and the chloroform area corrected to the same molar area as the bromotrichloromethane (correction factor, $BrCCl_3/HCCl_3 = 1.18$). The decrease in the bromotrichloromethane area was the total bromotrichloromethane reacted. The corrected chloroform area was taken as the amount of this bromotrichloromethane involved in the hydrogen abstraction reaction. The difference in the decrease in the bromotrichloromethane area and the corrected chloroform area was the amount of bromotrichloromethane that reacted in the addition reaction. Typical data are shown in Table II.

TABLE II

Gas Chromatographic Data Collected to Determine $k_a/k_t$

| | | | Areas (Cm.$^2$) | | | | |
|---|---|---|---|---|---|---|---|
| | | | $BrCCl_3$ | | $HCCl_3$ | | |
| Olefin | Temp. | Run | Before | After | Found | Corrected | $k_a/k_t$ |
| 3-Heptene | 77.8 | 3 | 42.0 | 31.2 | 2.0 | 2.4 | 3.5 |
| | 77.8 | 4 | 39.5 | 20.9 | 3.5 | 4.2 | 3.4 |
| Cycylpentene | 40.0 | 2 | 43.1 | 6.6 | 4.1 | 4.9 | 6.4 |
| | 40.0 | 4 | 54.8 | 20.0 | 3.8 | 4.6 | 6.6 |

The reactions with the 2-butenes were carried out in the presence of benzene which served as an internal standard for the gas chromatographic analyses of the reaction mixtures.

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Lawrence, Kan.

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[Contribution from the Phillips Petroleum Co.]

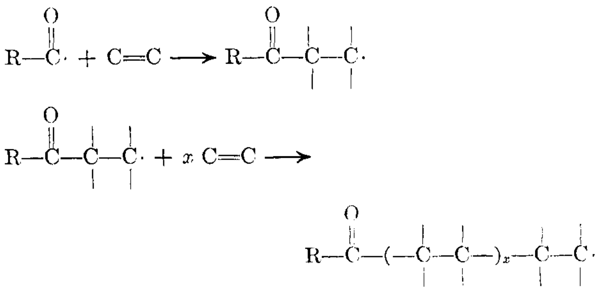
# The Radiation-Induced Reaction of Aldehydes with Olefins

C. E. STOOPS and C. L. FURROW

*Received December 27, 1960*

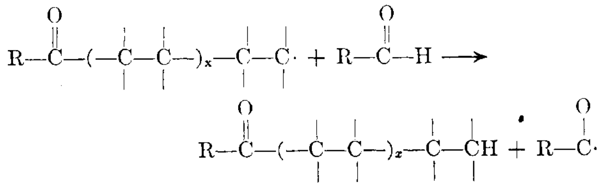
The radiation-induced reaction of aldehydes with olefins yields low molecular weight ketones by a chain process in which the acyl radical derived from the aldehyde adds to an olefin molecule with subsequent chain growth or with chain transfer to regenerate the acyl radical. Reactivity declines progressively in the series acetaldehyde, propionaldehyde, isobutyraldehyde, trimethylacetaldehyde, and also in the series ethylene, propylene, *trans*-butene-2, *cis*-butene-2, isobutylene. Quantitative estimation of yield was made by conversion of each product mixture to 2,4-dinitrophenylhydrazones followed by spectrophotometric determination of the individual quantities of each derivative after separation by paper chromatography. Conclusions regarding structure-reactivity relations are made.

The preparation of ketones by the free radical addition of aldehydes to olefins, with the acyl radical effectively the chain-carrying species, has been recognized for some time.[1]



$$R-\overset{\overset{O}{\|}}{C}\cdot + C{=}C \longrightarrow R-\overset{\overset{O}{\|}}{C}-\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}\cdot$$

$$R-\overset{\overset{O}{\|}}{C}-\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}\cdot + x\,C{=}C \longrightarrow R-\overset{\overset{O}{\|}}{C}-(-\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}-)_x-\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}\cdot$$



$$R-\overset{\overset{O}{\|}}{C}-(-\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}-)_x-\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}\cdot + R-\overset{\overset{O}{\|}}{C}-H \longrightarrow R-\overset{\overset{O}{\|}}{C}-(-\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}-)_x-\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}H + R-\overset{\overset{O}{|}}{C}\cdot$$

The predominant radiation-induced reaction of aldehydes with olefins has been found to follow the same course.[2] Structure-reactivity relations were

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[1] Cheves Walling, *Free Radicals in Solution*, Wiley New York, 1957, pp. 273–278.

[2] Since completion of this work a report has appeared concerning the radiation-induced addition of aldehydes to esters of unsaturated acids: R. H. Wiley and J. R. Harrell, *J. Org. Chem.*, **25**, 903 (1960).

observed among simple, methyl-substituted acetaldehydes and ethylenes. The acetaldehyde-ethylene system served as a baseline.

Irradiations were carried out in stainless steel bombs at approximately 30° to a total dose of $10^7$ r. The irradiations were made, using spent fuel elements, at the Gamma Facility, Materials Testing Reactor, Idaho Falls, Idaho. In early experiments some product mixtures were separated by distillation with subsequent product identification by derivative melting point. However, reliable quantitative data were not obtained, particularly for products produced in low yield. Quantitative data were obtained by separating the 2,4-dinitrophenylhydrazones of the ketones in each mixture of irradiation products by paper chromatography with standardization by authentic derivative samples. This method does not ordinarily[3] separate derivatives of isomers, but it does not impede showing structure-reactivity relations among aldehydes and olefins. Division between isomeric products from the respective reactions of propylene and isobutylene is the only information not revealed by this method. Isomers arise because these olefins are not symmetrical about the double bond.

*Effect of methyl substitution in the aldehyde.* Increasing methyl substitution results in declining product yields (Table I). The comparative reactivities[4] of the aldehydes are reflected in the G(−ethylene) values—*i.e.*, the number of moles of ethylene used in ketone formation per 100 e.v. absorbed. The G(+ketone) values, the number of ketone molecules formed per 100 e.v. absorbed, are shown below each formula in Table I and reveal the decreased yield with increased molecular weight within each series.

In order to discuss comparative reactivities of the aldehydes in terms of the G(−ethylene) values, it must be established that the aldehydes do not significantly decompose under existing conditions in a manner independent of the reaction sequence shown above. Indeed, it is well known that aldehyde decomposition by deformylation becomes increasingly important with greater branching at the α-carbon atom. This suggests that the trend in ketone yields may simply reflect the increased instability of the higher aldehydes. Deformylation would yield an alkyl radical which might then be expected to react with ethylene to yield hydrocarbon telomers.[5] Thus, isobutyraldehyde decomposition (accompanying Reaction C, Table I) would lead to the formation of 2-methylbutane and 2-methylhexane. Trimethylacetaldehyde (Reaction D, Table I) would correspondingly lead to 2,2-dimethylbutane and 2,2-dimethylhexane. However, an examination by vapor phase chromatography of the product mixture from Reaction C failed to detect 2-methylbutane or 2-methylhexane. Similarly, v.p.c. did not detect 2,2-dimethylbutane among the products of Reaction D. However, a peak corresponding to 2,2-dimethylhexane was observed. Injection of a standard sample did not distort this peak. This peak would represent sufficient 2,2-dimethylhexane to account for only 1.97% of the trimethylacetaldehyde charged. Additional evidence for the absence of large scale deformylation was obtained by preparation of derivatives from all of the distillation fractions as well as the undistilled residues. In Reaction C, 2.1% of the isobutyraldehyde was represented in the various products and 90.5% remained unchanged thus accounting for a total of 92.6% of the isobutyraldehyde charged. Similarly, 20.1% of the trimethylacetaldehyde was represented in the various products of Reaction D and 70.0% as unchanged aldehyde to account for 90.1% of the original charge. The aldehyde unaccounted for in each case represents decomposition to volatile products plus mechanical losses. Accurate material balance data on the other aldehydes and on the olefins were not sought. Clearly, deformylation does not consume a major portion of the branched aldehydes under these conditions and does not offer a basis on which to explain the relative G(−ethylene) values. The existence of acyl radicals of stability sufficient to permit their being "trapped" by olefin molecules is implicit in the observed products and yields.

The acyl radicals may be produced in a primary step or they may be a result of secondary reactions. If acyl radical production is a primary step, it is logical to assume that the yield of acyl radicals would be independent of structure for the limited molecular weight range studied. Thus, the number of chains initiated would be also independent of structure. However, the data (Table I) show an unmistakable decrease in the number of chains[6] initiated with higher aldehydes. This suggests that acyl radical production is not a primary process. Perhaps the initial reaction in aldehyde radiolysis is the separation of a hydrogen atom[7] carrying excess energy.[8] This atom, upon collision with a substrate

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[3] It does separate 4-methyl-2-pentanone from other $C_6$ ketones (see Table IV). However, they are not co-product with 4-methyl-2-pentanone (in reaction H, Table II).

[4] By "reactivity" is meant the total ability of the compound to contribute to the yield of final product. It does not refer *exclusively* to the facility with which an aldehyde molecule undergoes homolytic bond cleavage or to the affinity of an olefin molecule for an acyl radical but does include these initial effects as they contribute to the observed over-all result.

[5] Cheves Walling, *Free Radicals in Solution*, Wiley, New York, 1957, pp. 277–279.

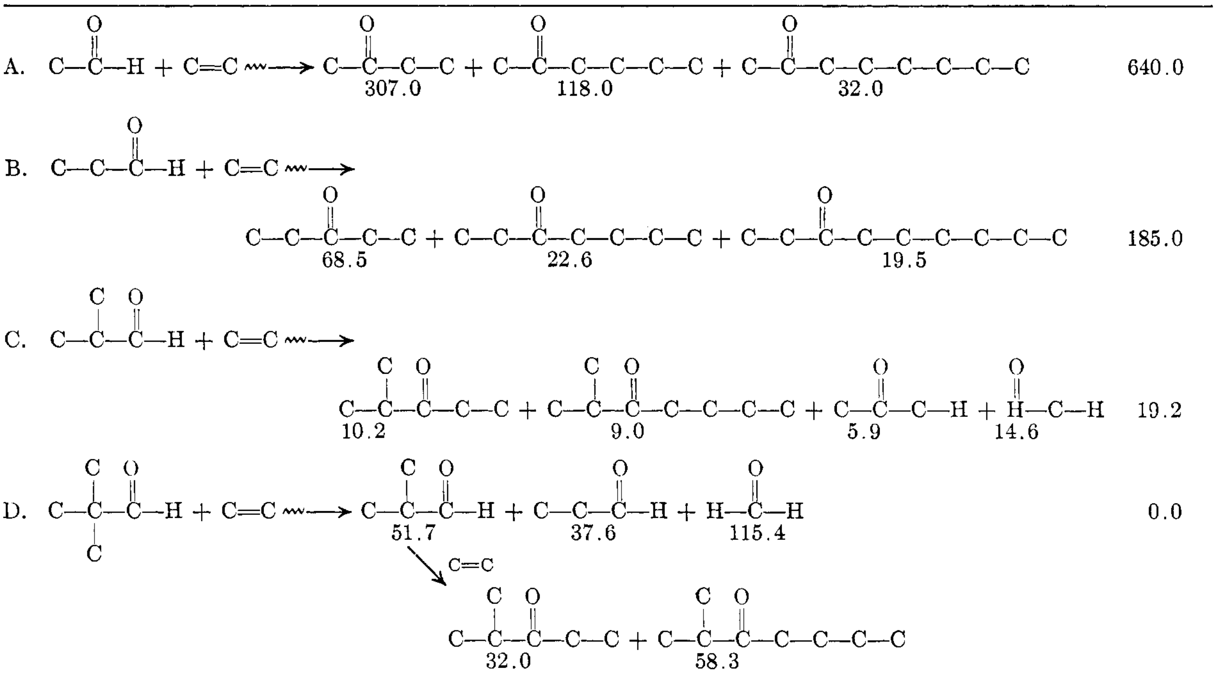
[6] The accurate determination of the number of chains initiated in each reaction was not undertaken. The fact that a maximum of two or three ethylene molecules is added indicates a similar chain transfer efficiency among the aldehydes and indicates that the widely divergent G($-C_2H_4$) values reflect decided differences between the number of chains initiated.

[7] Not necessarily the formyl hydrogen atom.

[8] Analogous to the conclusions of P. Ausloss and P. F. Paulson, *J. Am. Chem. Soc.*, **80**, 5117 (1958) regarding ketone radiolysis.

TABLE I

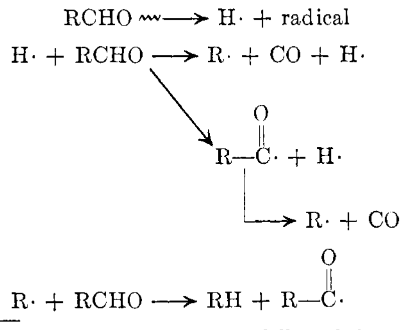
Effect of Methyl Substitution in the Aldehyde[a]



| | | $G(-C_2H_4)$ |
|---|---|---|
| A. | $\mathrm{C{-}\overset{O}{\overset{\|}{C}}{-}H + C{=}C \rightsquigarrow \underset{307.0}{C{-}\overset{O}{\overset{\|}{C}}{-}C{-}C} + \underset{118.0}{C{-}\overset{O}{\overset{\|}{C}}{-}C{-}C{-}C{-}C} + \underset{32.0}{C{-}\overset{O}{\overset{\|}{C}}{-}C{-}C{-}C{-}C{-}C{-}C}}$ | 640.0 |
| B. | $\mathrm{C{-}C{-}\overset{O}{\overset{\|}{C}}{-}H + C{=}C \rightsquigarrow \underset{68.5}{C{-}C{-}\overset{O}{\overset{\|}{C}}{-}C{-}C} + \underset{22.6}{C{-}C{-}\overset{O}{\overset{\|}{C}}{-}C{-}C{-}C{-}C} + \underset{19.5}{C{-}C{-}\overset{O}{\overset{\|}{C}}{-}C{-}C{-}C{-}C{-}C{-}C}}$ | 185.0 |
| C. | $\mathrm{C{-}\overset{C}{\overset{\vert}{C}}{-}\overset{O}{\overset{\|}{C}}{-}H + C{=}C \rightsquigarrow \underset{10.2}{C{-}\overset{C}{\overset{\vert}{C}}{-}\overset{O}{\overset{\|}{C}}{-}C{-}C} + \underset{9.0}{C{-}\overset{C}{\overset{\vert}{C}}{-}\overset{O}{\overset{\|}{C}}{-}C{-}C{-}C{-}C} + \underset{5.9}{C{-}\overset{O}{\overset{\|}{C}}{-}C{-}H} + \underset{14.6}{H{-}\overset{O}{\overset{\|}{C}}{-}H}}$ | 19.2 |
| D. | $\mathrm{C{-}\underset{\underset{C}{\vert}}{\overset{C}{\overset{\vert}{C}}}{-}\overset{O}{\overset{\|}{C}}{-}H + C{=}C \rightsquigarrow \underset{51.7}{C{-}\overset{C}{\overset{\vert}{C}}{-}\overset{O}{\overset{\|}{C}}{-}H} + \underset{37.6}{C{-}C{-}\overset{O}{\overset{\|}{C}}{-}H} + \underset{115.4}{H{-}\overset{O}{\overset{\|}{C}}{-}H}}$<br>$\mathrm{\xrightarrow{C=C} \underset{32.0}{C{-}\overset{C}{\overset{\vert}{C}}{-}\overset{O}{\overset{\|}{C}}{-}C{-}C} + \underset{58.3}{C{-}\overset{C}{\overset{\vert}{C}}{-}\overset{O}{\overset{\|}{C}}{-}C{-}C{-}C{-}C}}$ | 0.0 |

[a] Individual G(+product) values are indicated as subscripts.

aldehyde molecule, could cause cleavage at the alkyl-formyl bond or alternatively abstract the formyl hydrogen atom yielding an activated acyl radical. This would readily decarbonylate to an alkyl radical. Acyl radical formation would occur in a subsequent step.[9]



$$\mathrm{RCHO} \rightsquigarrow \mathrm{H\cdot + radical}$$
$$\mathrm{H\cdot + RCHO \longrightarrow R\cdot + CO + H\cdot}$$
$$\searrow \mathrm{R{-}\overset{O}{\overset{\|}{C}}\cdot + H\cdot} \longrightarrow \mathrm{R\cdot + CO}$$
$$\mathrm{R\cdot + RCHO \longrightarrow RH + R{-}\overset{O}{\overset{\|}{C}}\cdot}$$

This mechanism involves trace hydrocarbon formation. The gaseous products were not examined and direct experimental evidence cannot be used in evaluating this mechanism as a possible chain initiating sequence. An indirect argument for this mechanism could be based on the decrease in the number of chains initiated in ascending the aldehyde series. While the primary step is independent of aldehyde structure[18] the alkyl radicals which result (methyl, ethyl, isopropyl, and *t*-butyl, respectively) decline in reactivity—*i.e.*, are less apt to propagate chain growth or undergo chain transfer. The trend in gross reactivity observed in the $G(-C_2H_4)$ values would be predictable from the relative reactivity of the alkyl radicals if the generation of the initial acyl radicals in each system depends on the intermediate formation of alkyl radicals. The difference in reactivity between acetaldehyde and propionaldehyde as seen in $G(-C_2H_4)$ data is consistent with the apparent stabilization of the ethyl radical over the methyl radical as indicated by relative bond dissociation energies for $CH_3$—H, 102 kcal./mole[19–23]; and $C_2H_5$—H, 98 kcal./mole.[24,25]

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(9) Alkyl-formyl bond cleavage followed by aldehyde formyl hydrogen abstraction by this alkyl radical to generate an acyl radical would be similar in effect to the mechanism derived for gas phase photolysis.[10–17]

(10) C. J. Danby and C. N. Hinshelwood, *Proc. Roy. Soc.*, **A179**, 169 (1941).

(11) F. E. Blacet, *J. Phys. and Colloid Chem.*, **52**, 534 (1948).

(12) F. E. Blacet and J. G. Calvert, *J. Am. Chem. Soc.*, **73**, 661, 667 (1951).

(13) F. E. Blacet and J. N. Pitts, Jr., *J. Am. Chem. Soc.*, **74**, 3382 (1952).

(14) F. E. Blacet and R. E. Crane, *J. Am. Chem. Soc.*, **76**, 5337 (1954).

(15) J. G. Calvert, J. N. Pitts, Jr., and D. D. Thompson, *J. Am. Chem. Soc.*, **78**, 4239 (1956).

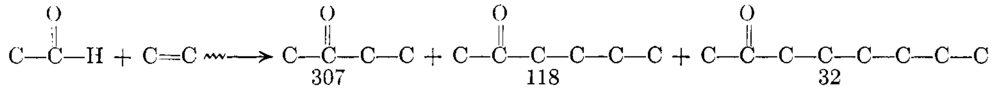
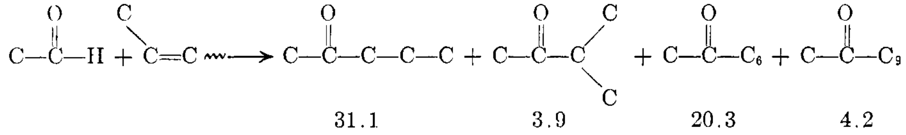
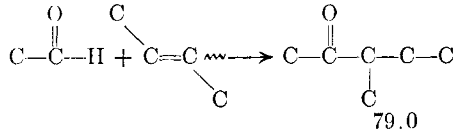
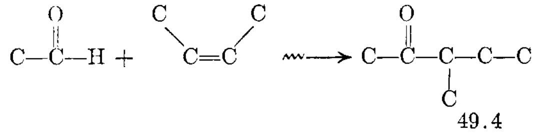
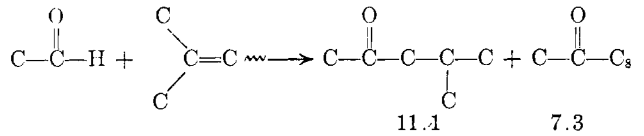
(16) J. A. Kerr and A. F. Trotman-Dickenson, *Trans. Faraday Soc.*, **55**, 572, 921 (1959).

(17) J. A. Kerr and A. F. Trotman-Dickenson, *J. Chem. Soc.*, 1602, 1611 (1960).

(18) Blacet and Pitts[13] have observed that the differences in photolytic susceptibility among the aldehydes is very small and declines with increasing energy of the radiation employed. From extrapolation to the gamma ray portion of the spectrum it would follow that the aldehydes would cleave with effectively equal ease.

TABLE II

Effect of Methyl Substitution in the Olefin[a]

| | | G(−Olefin) |
|---|---|---|
| A. |  | 640 |
| E. |  | 88.1 |
| F. |  | 79.0 |
| G. |  | |
| H. |  | 25.6 |

[a] Individual G(+product) values are indicated as subscripts.

The highly branched aldehydes are subject to dealkylation at the $\alpha$-carbon atom. Demethylation of isobutyraldehyde to propionaldehyde and formaldehyde was observed (Table I). The $G(-C_2H_4)$ value for the ethylene-trimethylacetaldehyde system is taken as zero since ethylene did not react with trimethylacetaldehyde although it did react with isobutyraldehyde produced by demethylation. The absence of acetaldehyde as a demethylation product is consistent with the observed radiation stability of propionaldehyde. Lower aldehydes generated by demethylation would also be expected to react with ethylene to contribute additional products. The formation of 2-methyl-3-pentanone and 2-methyl-3-heptanone (isobutyraldehyde products) from the trimethylacetaldehyde-ethylene system confirmed this. However, the propionaldehyde produced in this same system and that generated in the isobutyraldehyde ethylene irradiation failed to react measurably with ethylene (Table I). Secondary radiolysis effects were not explored, but it is quite probable that the quantities of propionaldehyde generated were simply too small to afford products in detectable yields.

Irradiation of a chloral-ethylene system did not yield trichloromethyl ketones. This result is not surprising in view of the electronegativity of the chlorine atoms (which would decrease the electron density at the carbonyl carbon atom of chloral thereby impeding formation of the trichloroacetyl radical and decreasing its reactivity to the extent that the radical formed). Patrick[26] similarly observed the failure of chloral to add to ethyl maleate in the presence of peroxides.

*Effect of methyl substitution in the olefin.* Ethylene reacts with acetaldehyde in higher yield than any of the methyl-substituted ethylenes (Table II). The reactivity order is indicated by the G(−olefin) values. As mentioned above derivatives of isomers are not usually separated by the chromatographic method. The nonspecific formulas indicate the possible existence of more than one isomer. The molecular weight represented in each mixture of isomeric derivatives was readily indicated by agreement in migration rate with one of a series of known derivatives. However, the mixed methyl propyl ketones arising in the acetaldehyde propylene reaction were separated by vapor phase chromatography, using polyethylene glycol as the liquid substrate, and the division was found to be 7.95/1

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(19) H. C. Andersen, G. B. Kistiakowski, and E. R. Van Artsdalen, *J. Chem. Phys.*, **10**, 305 (1942).

(20) H. C. Andersen and G. B. Kistiakowski, *J. Chem. Phys.*, **11**, 6 (1943).

(21) E. R. Van Artsdalen and G. B. Kistiakowski, *J. Chem. Phys.*, **12**, 28 (1944).

(22) D. P. Stevenson, *Discussions Faraday Soc.*, **10**, 35 (1951).

(23) C. A. McDowell and B. G. Cox, *J. Chem. Phys.*, **20**, 1496 (1952).

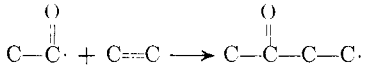
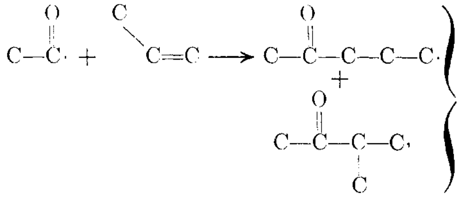
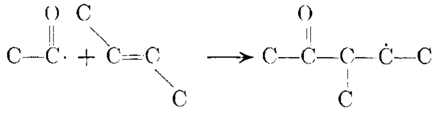
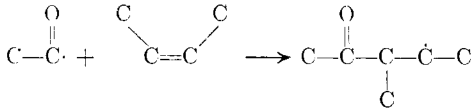
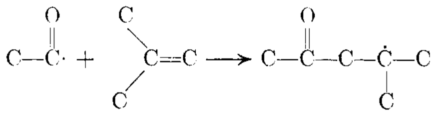
(24) C. H. Leigh and M. Swarc, *J. Chem. Phys.*, **20**, 844 (1952).

(25) J. B. Farmer and E. P. Lossing, *Can. J. Chem.*, **33**, 861 (1955).

(26) T. M. Patrick, Jr., *J. Org. Chem.*, **17**, 1009 (1952).

TABLE III

RELATION OF RADICAL INTERMEDIATES TO G(—OLEFIN)

| | G(—Olefin) |
|---|---|
|  $\mathrm{C{-}\overset{O}{\overset{\Vert}{C}}\cdot + C{=}C \longrightarrow C{-}\overset{O}{\overset{\Vert}{C}}{-}C{-}C\cdot}$ | 640.0 |
|  $\mathrm{C{-}\overset{O}{\overset{\Vert}{C}}\cdot + C{-}C{=}C \longrightarrow C{-}\overset{O}{\overset{\Vert}{C}}{-}C{-}C{-}C\cdot + C{-}\overset{O}{\overset{\Vert}{C}}{-}\underset{C}{C}{-}C\cdot}$ | 88.1 |
|  $\mathrm{C{-}\overset{O}{\overset{\Vert}{C}}\cdot + C{-}C{=}C{-}C \longrightarrow C{-}\overset{O}{\overset{\Vert}{C}}{-}\underset{C}{C}{-}\dot{C}{-}C}$ | 79.0 |
|  $\mathrm{C{-}\overset{O}{\overset{\Vert}{C}}\cdot + C{-}C{=}C{-}C \longrightarrow C{-}\overset{O}{\overset{\Vert}{C}}{-}\underset{C}{C}{-}\dot{C}{-}C}$ | 49.4 |
|  $\mathrm{C{-}\overset{O}{\overset{\Vert}{C}}\cdot + (C)_2C{=}C \longrightarrow C{-}\overset{O}{\overset{\Vert}{C}}{-}C{-}\underset{C}{\dot{C}}{-}C}$ | 25.6 |

in favor of the normal isomer. This preference for 2-pentanone over 3-methyl-2-butanone is expected in view of the polarizing effect of the methyl group on the propylene double bond.

The clear-cut superiority of ethylene sets it apart from other olefins which, in general, exhibit very little free radical chemistry. The other olefins each possess allyl hydrogen atoms. The limited free-radical reactivity of such compounds is generally ascribed to the facile formation of resonance-stabilized allyl radicals by the abstraction of allyl hydrogen atoms. The G(−olefin) valuesd ecline in parallel with a trend from primary to secondary to tertiary keto radicals formed as initial addition products (Table III). Declining keto-radical reactivity would be expected to manifest itself in reduced chain-transfer efficiency toward acetaldehyde and in less chain propagation.

Analytical accuracy, established on known compositions, is ± 10 % of the amount present. The agreement in G(−propylene) and G(−*trans*-butene-2) values is surprising. No explanation is advanced for this relation or for the difference between the G values for the disappearance of *cis*- and *trans*-butene-2. However, since the same keto radical is formed by the addition of an acetyl radical to either isomer, any difference in product yield would seem traceable to differences in the relative affinity of the isomers toward the acetyl radical. While this point has not been explored, Szwarc *et al.*[27] have observed a similarly greater reactivity of *trans*- over *cis*-butene-2 in their determinations of methyl affinities.

## EXPERIMENTAL

*Irradiation mixtures.* A standard charge of 2 moles of aldehyde and one of olefin was employed in each irradiation except with trimethylacetaldehyde-ethylene in which 1 mole of each was charged. The aldehyde was placed in a stainless steel American Instrument Company Micro Series reaction vessel of approximately 300 ml. volume. The bomb, chilled to −78°, was evacuated and flushed with the olefin; evacuation and flushing were repeated three times; the required amount of olefin was distilled into the evacuated bomb. The aldehydes were Eastman white label (excepting trimethylacetaldehyde which was obtained from Columbia Organic Chemicals Company, Inc.) and the olefins were Phillips pure grade. Irradiations were made at approximately 85°F to a total dose of $10^7$ r using spent fuel elements at the Gamma Facility, Materials Testing Reactor, Idaho Falls, Idaho. The products were identified by mass spectrometry, in part by derivative melting point[28] and through the procedure described below which also supplied quantitative data on reaction yields.

*Quantitative determination of yields.* Adaptations of the methods of Iddles and Jackson[29] for the quantitative preparation of 2,4-dinitrophenylhydrazones and of Buyske *et al.*[30] for the separation and quantitative determination of 2,4-dinitrophenylhydrazones were developed.

A mixture of 1.6 g. of 2,4-dinitrophenylhydrazine in 400 ml. of 2*N* hydrochloric acid was stirred for 30 min., cooled

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[27] R. P. Buckley, F. Leavitt, and M. Szwarc, *J. Am. Chem. Soc.*, **78**, 5557 (1956).

[28] The ketones identified by derivative melting points specifically established that acetaldehyde produced methyl ketones, propionaldehyde produced ethyl ketones, as required by the over-all reaction scheme.

[29] H. A. Iddles and C. E. Jackson, *Ind. and Eng. Chem., Anal. Ed.*, **6**, 454 (1934).

[30] D. A. Buyske, L. H. Owen, P. Wilder, and M. E. Hobbs, *Anal. Chem.*, **28**, 910 (1956).

TABLE IV

| Carbonyl Compounds, Name | Source of Product, Authentic Derivative | | | Derivative, M.P.[j] | |
|---|---|---|---|---|---|
| | Reaction[b] | Sample[c] | $R_f$ | Found | Lit. |
| (2,4-Dinitrophenylhydrazine) | | Eastman | (0.00) | | |
| Formaldehyde | C, D | Eastman[d] | 0.05 | | |
| Acetaldehyde | | Eastman | 0.09 | | |
| Propionaldehyde | C, D | Eastman | 0.13 | | |
| Isobutyraldehyde | D | Eastman | 0.20 | | |
| Trimethylacetaldehyde | | Columbia Org. Chem. Co., Inc. | 0.24 | | |
| 2-Butanone | A | Eastman | 0.21 | 109–110 | 107–109[k] |
| 2-Pentanone | E | Delta Chemical Works | 0.28 | | |
| 3-Methyl-2-butanone | E | Eastman | 0.30 | | |
| 3-Pentanone | B | Eastman | 0.30 | 155–155.5 | 156[l] |
| 2-Hexanone | A | K and K Laboratories, Inc. | 0.37 | 105–105.5 | 106[l] |
| 4-Methyl-2-pentanone | H | Eastman | 0.30 | 94 | 95[l] |
| 2-Methyl-3-pentanone | C, D | Synthesized[e] | 0.42 | | |
| 3-Methyl-2-pentanone | F, G | Synthesized[f] | 0.36 | | |
| 3-Heptanone | B | Delta Chemical Works | 0.51 | | |
| 2-Octanone | A | Eastman | 0.56 | 57 | 58[l] |
| 6-Methyl-2-heptanone[a] | E | Delta Chemical Works | 0.56 | | |
| 2-Methyl-3-heptanone | C | Synthesized[g] | 0.65 | | |
| 3-Methyl-2-heptanone[a] | E | Synthesized[h] | 0.56 | | |
| 3,5-Dimethyl-2-hexanone | E | Synthesized[i] | 0.56 | | |
| 2-Nonanone[a] | B | Eastman | 0.70 | | |
| 2-Decanone[a] | H | K and K Laboratories, Inc. | 0.78 | | |
| 2-Undecanone[a] | E | Eastman | 0.85 | | |

[a] Representative isomers, adequate for identification in terms of mol. wt. since chromatographic method does not precisely separate isomers. [b] See Tables I and II. [c] Commercially obtained samples were fractionated (Podbielniak Mini-Cal Heli-Grid column), center cuts retained. [d] Prepared from paraformaldehyde. [e] Synthesized, ref. R. B. Wagner and J. A. Moore, *J. Am. Chem. Soc.*, **72,** 974 (1950). [f] Synthesized by acetoacetic ester method. [g] Synthesized, ref. J. Cason and M. P. Chang, *J. Org. Chem.* **21,** 449 (1956). [h] Synthesized, ref. S. G. Powell, *J. Am. Chem. Soc.*, **46,** 2515 (1924). [i] Synthesized, ref. H. Haeussler and J. Dijkima, *Ber.*, **77,** 601 (1944) followed by reduction with $H_2$, Pd(C). [j] Uncorrected. [k] C. H. Stitler and J. R. Little, U. S. Pat. **2,517,732** (August 8, 1950) to U. S. Rubber Co. Another lit. m.p. 117°[l] could not be obtained. [l] R. L. Shriner, R. C. Fuson, and D. Y. Curtin, *The Systematic Identification of Organic Compounds,* Fourth ed., Wiley, New York, 1956, p. 316.

to 0°, and any undissolved 2,4-dinitrophenylhydrazine was filtered from the saturated solution. The solution contained 7.6–8.1 mmoles of 2,4-dinitrophenylhydrazine. An accurately weighed sample of approximately 0.2 g. of the irradiation product mixture, which had been previously concentrated by distillation to remove unchanged aldehyde, was added to the solution. The 0.2-g. sample would contain 4.54 mmoles if the average molecular weight was that of acetaldehyde to give a minimum of 67% excess of 2,4-dinitrophenylhydrazine. (Reactions C and D [Table I] were found to yield carbonyl compounds of lower molecular weight than the aldehyde charged and in these the distillates were also sampled for complete yield data.) This admixture was allowed to stand at 0°; it was filtered at the end of 4 hr. and once daily thereafter until derivative formation was complete. Four days were the maximum required. The mixed 2,4-dinitrophenylhydrazones were dried over phosphorus pentoxide at reduced pressure. They were separated by paper chromatography using *n*-hexane and *N,N*-dimethylformamide as the solvent pair. The percentage composition of the derivative mixture was established by elution of the separate spots with methanol followed by spectrophotometric determination of the amount present at each spot. (The spots were identified through comparative migration rates using authentic derivative samples which were applied with the analytical sample on the same sheet of paper.) These values were converted to the corresponding values for the composition of the original mixture of ketones using the factor $\frac{\text{mol. wt. of ketone}}{\text{mol. wt. of derivative}}$. The composition values for the ketone mixture were normalized to total 100% to compensate for the quantity of excess 2,4-dinitrophenylhydrazine present in the derivative mixture. (2,4-Dinitrophenylhydrazine does not migrate under the above conditions.) The quantities of the individual ketones were determined from these data and from the total weight of ketone mixture. The results were used to calculate radiation yields.

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