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# Free Radical Displacement Processes: Reactions of $CH_3$ and $CD_3$ Radicals with Crotonaldehyde and with Methyl Propenyl Ketone[1]

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Confirmatory evidence for the free radical displacement $CH_3 + CH_3CH{=}CHCOCH_3 = C_4H_8 + CH_3CO$ was obtained when photolysis of a mixture of acetone-$d_6$ and *trans*-methyl propenyl ketone gave as a product 2-butene consisting of 78% $CD_3CH{=}CHCH_3$ and 22% $CH_3CH{=}CHCH_3$. The analogous displacement $CH_3 + CH_3CH{=}CHCHO = C_4H_8 + HCO$, reaction 1, occurred when mixtures of acetone and crotonaldehyde were photolyzed at 2654 Å., and temperatures from 120 to 350°. At 120° the over-all quantum yields were much less than unity, but at 350° they were $CO = 11$, $C_3H_6 = 5.5$, $C_4H_8 = 0.43$, $H_2 = 0.28$ and $CH_4 < 2$. Alternative mechanisms for the chain production of CO and $C_3H_6$ are presented. $CD_3$ radicals were generated in the presence of crotonaldehyde, and, in confirmation of reaction 1, the butene was exclusively $CD_3CH{=}CHCH_3$. "Hot" methyl radicals or photo-excited crotonaldehyde molecules are not essential for (1) since pyrolysis of mixtures of di-*t*-butyl peroxide and crotonaldehyde at 170° gave 2-butene as a major product.

In a recent study of the reactions of methyl radicals with *trans*-methyl propenyl ketone,[2,3] it was necessary to postulate the free radical displacement process (1) to explain adequately the results. Although considerable evidence for (1)

$$CH_3 + CH_3CH{=}CHCOCH_3 \longrightarrow CH_3CH{=}CHCH_3 + CH_3CO \quad (1)$$

was accumulated, it was, in a sense, indirect. A direct test of (1) was proposed[4] in which $CD_3$ radicals would be allowed to react with the ketone and the products would be analyzed for $CD_3CH{=}CHCH_3$. This paper reports the results of this study and of its extension to include reactions of methyl radicals with crotonaldehyde.

## Experimental

**Apparatus.**—All photolyses and pyrolyses were carried out in the same reaction system.[2] The cylindrical reaction cell was made of fused quartz, 20.0 cm. long, 30.0 mm. i.d.; it had a volume of 140 cc. The cell was almost filled with a parallel beam of radiation. Most photochemical runs were made with a Type A Hanovia quartz-mercury arc followed by a quartz cell filled with a $Br_2$–$Cl_2$ mixture that transmitted, in the ultraviolet, chiefly 2654 Å. and 2537 Å. radiation. The reaction cell was placed in a metallic block oven with automatic temperature control. The fraction of light transmitted was measured with an RCA 935 phototube while absolute light intensities were determined by using acetone photolysis at 120° as an internal actinometer. Other apparatus was of conventional design.

**Materials.**—The *trans*-methyl propenyl ketone was prepared by the action of dimethylcadmium on crotonoyl chloride. After three distillations the product gave $n^{25}D$ 1.4320 (I.C.T., $n^{20}D$ 1.4350, $n^{15}D$ 1.4370). The crotonaldehyde was Eastman, white label, dried and distilled at a high reflux rate through a spinning band column. For the distillate, $n^{20}D$ 1.4367 (Beilstein I-728, $n^{20.5}D$ 1.4362). Acetone was Mallinckrodt Reagent grade, while the di-*t*-butyl peroxide, furnished through the courtesy of the Shell Development Company, was purified by bulb to bulb distillation. Acetone-$d_6$ with isotopic purity in excess of 99% was kindly supplied by Dr. J. R. McNesby.

**Analytical Methods.**—At the end of each run the products and unreacted starting materials were cooled to $N_2$ (liquid) temperature and the CO, $CH_4$ and $H_2$ removed with a Toepler pump. The remaining material was then separated, with the aid of a modified Ward–LeRoy still, into fractions volatile at −150° (primarily propylene) and at −128° (butene). A portion of the $C_1$ cut was analyzed for CO with a Blacet–Leighton microgas analysis apparatus. The remainder of the $C_1$ cut and the second and third fractions were analyzed with a mass spectrometer. Analysis of deuterated compounds was complicated by the lack of pure standards and most of these analyses must be considered to be only semi-quantitative. The parent peak of $CD_3CH{=}CHCH_3$ was considered to have the same sensitivity as $CH_3$-$CH{=}CHCH_3$.

## Results

For equal pressures of the two compounds, acetone absorbs about three-fourths and methyl propenyl ketone one-fourth of the incident 2654–2537 radiation. The quantum yields reported in Table I represent the total yields of product per total quanta absorbed by the two ketones. Similar considerations apply for the results of photolyses of crotonaldehyde–acetone mixtures in Table II. Corrections were made for dark reactions, but these were large only for the photolysis of acetone–crotonaldehyde mixtures at 350° where the corrections were about 15% for CO and 25% for propylene. No dark correction was needed for the 2-butene at 350°.

**A. *trans*-Methyl Propenyl Ketone.**—Over-all quantum yields for the photolysis of mixtures of *trans*-methyl propenyl ketone with acetone or perdeuteroacetone are

TABLE I

QUANTUM YIELDS OF NON-CONDENSABLE PRODUCTS FROM THE PHOTOLYSIS OF MIXTURES OF METHYL PROPENYL KETONE WITH ACETONE OR WITH PERDEUTEROACETONE AT 2654–2537 Å. AND 170°

| | Run 1 | Run 2 |
|---|---|---|
| Pressure, MPK mm. | 46.5 | 46.0 |
| Pressure of acetone, mm. | 39.5 | 0.00 |
| Pressure of acetone-$d_6$, mm. | 0.00 | 42 |
| Time, sec. | 6500 | 6550 |
| $I_a$, (quanta abs./cc. sec.) $\times 10^{-12}$ | 9.84 | 9.84 |
| Over-all quantum yields | | |
| CO | 0.98 | 0.99 |
| 2-Butene | 0.22 | .047 |
| $CD_3CH{=}CHCH_3$ | ... | .165 |
| Total butene | 0.22 | .21 |
| $CH_4$ | [a] | .018 |
| $CD_3H$ | ... | .071 |
| $CH_3CH_3$ | [a] | .009 |
| $C_2D_6$ | ... | .036 |
| $CD_3CH_3$ | ... | .010 |
| Propylene | Trace | Trace |

[a] Present but not determined.

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(1) Presented before the Division of Physical and Inorganic Chemistry, at the Spring meeting of the American Chemical Society, Miami, Fla., 1957. Taken in part from the senior thesis submitted for the A.B. degree by D. D. Thompson.

(2) J. N. Pitts, Jr., R. S. Tolberg and T. W. Martin, THIS JOURNAL, **76**, 2834 (1954).

(3) J. N. Pitts, Jr., R. S. Tolberg and T. W. Martin, *ibid.*, **79**, 6370 (1957).

(4) J. N. Pitts, Jr., Conference on Photochemistry and Free Radicals, University of Rochester, September, 1954.

TABLE II

OVER-ALL QUANTUM YIELDS OF NON-CONDENSABLE PRODUCTS FROM THE PHOTOLYSIS OF MIXTURES OF CROTONALDEHYDE AND ACETONE AT 2654–2537 Å. AND A SERIES OF TEMPERATURES

| Run | Temp., °C. | Pressure crotonaldehyde, mm. | Pressure acetone, mm. | Time, sec. $\times 10^{-3}$ | $I_a$, quanta abs. cc. sec. $\times 10^{-12}$ | Quantum yields CO | $C_3H_6$ | $C_4H_8$ | $H_2$ |
|---|---|---|---|---|---|---|---|---|---|
| 3 | 120 | 52 | 46.5 | 10.0 | 8.38 | 0.57 | [a] | 0.008 | 0.0045 |
| 4 | 170 | 51 | 39.5 | 9.01 | 7.99 | 1.41 | 0.13 | .14 | .0092 |
| 5 | 210 | 52 | 47 | 11.06 | 7.83 | 1.94 | .25 | .22 | .011 |
| 6 | 210 | 53 | 48 | 7.62 | 7.50 | 1.91 | .27 | .21 | [a] |
| 7 | 250 | 52 | 47 | 7.06 | 8.36 | 2.95 | .69 | .28 | .028 |
| 8 | 300 | 52 | 49 | 4.69 | 7.63 | 4.33 | 1.45 | .33 | .074 |
| 9 | 350 | 54 | 52 | 2.47 | 7.35 | 10.5 | 5.5 | .45 | [a] |
| 10 | 350 | 54 | 47 | 2.17 | 3.48 | 11.1 | 5.8 | .40 | .25 |
| 11 | 350 | 49 | 47 | 3.22 | 3.48 | 11.4 | 5.2 | .72 | .31 |

[a] Not determined.

deuteroacetone are given in Table I. No $CH_3D$ was found.

**B. Crotonaldehyde.**—Over-all quantum yields in the photolysis of crotonaldehyde–acetone mixtures at 2654–2537 Å. and a series of temperatures are given in Table II. The major products were CO, propylene, 2-butene and methane. Small, but significant yields of hydrogen were found. Methane and the traces of ethane were products but were not determined quantitatively. Carbon monoxide and propylene were produced by a chain process, since the over-all quantum yields were of the order of 11 and 5, respectively, at 350°. The value of $\Phi_{\text{Butene}}$ of 0.72 in run 11 is completely out of line with the other results. No explanation is apparent other than that it is a gross error. One photolysis at 250° was made under conditions similar to run 7 except that perdeuteroacetone was used. The following quantum yields were obtained: CO = 2.23; $C_3H_8$ = 0.60 (no deuterated propylene was detected); $CD_3CH{=}CHCH_3$ = 0.14 (no non-deuterated 2-butene was observed). The hydrogen-$C_1$ cut was lost.

A mixture of 15 mm. of di-*t*-butyl peroxide and 54 mm. of crotonaldehyde was heated for 13 minutes at 170°. The volumes of the major non-condensable products were CO = 647; $C_3H_6$ = 81; 2-butene = 101; $CH_4$ = 978; and $C_2H_6$ = 132 microliters S.T.P. Only a trace of hydrogen (less than 0.5 microliter) was observed.

## Discussion

***trans*-Methyl Propenyl Ketone.**—Results from the photolysis of mixtures of $CD_3COCD_3$ and *trans*-methyl propenyl ketone confirm previous postulates[2,3] of the existence of the free radical displacement process (1). This type of reaction seems necessary to explain the yields of 2-butene, and it is a key feature of the following mechanism for the formation of the non-condensable products. Because of the small quantum yields of decomposition, methyl propenyl ketone primary processes are neglected in this treatment.

$$CD_3COCD_3 + h\nu \longrightarrow 2CD_3 + CO \qquad (I)$$

$$CD_3 + CH_3CH{=}CHCOCH_3 \longrightarrow CH_3CH{=}CHCD_3 + CH_3CO \qquad (2)$$

$$CH_3CO \longrightarrow CH_3 + CO \qquad (3)$$

$$CH_3 + CH_3CH{=}CHCOCH_3 \longrightarrow CH_3CH{=}CHCH_3 + CH_3CO \qquad (1)$$

$$CD_3 + CH_3CH{=}CHCOCH_3 \longrightarrow CD_3H + CH_2CH{=}CHCOCH_3 \qquad (4)$$

$$CH_3 + CH_3CH{=}CHCOCH_3 \longrightarrow CH_4 + CH_2CH{=}CHCOCH_3 \qquad (5)$$

$$2CD_3 \longrightarrow C_2D_6 \qquad (6)$$

$$CD_3 + CH_3 \longrightarrow CD_3CH_3 \qquad (7)$$

$$2CH_3 \longrightarrow C_2H_6 \qquad (8)$$

Primary process (I) is well established for acetone and acetone-$d_6$ and at 170° the quantum yield of carbon monoxide may be taken as unity.[5,6] Perdeuteromethyl radicals formed in (I) may abstract H or D atoms from the substrate, recombine or react at the alpha or $\beta$-carbon atom of the olefinic double bond in the methyl propenyl ketone. This multiplicity of reactions leads to a complex mixture of condensable products which was not subjected to detailed analyses; however, several conclusions can be drawn from the observed yields of the non-condensable products.

(a) The large yield of $CD_3CH{=}CHCH_3$ compared to $CD_3H$, $C_2D_6$ and $CD_3CH_3$ indicates that under the experimental conditions employed, the displacement process (2) is favored over competing abstraction and disproportionation reactions of the methyl radicals. Most of the 2-butene is $CD_3CH{=}CHCH_3$, and the presence of the $CD_3$ group in this olefin is evidence against butene formation from a direct decomposition of *trans*-methyl propenyl ketone into 2-butene and CO. Furthermore, the large yield of 2-butene relative to the ethanes is evidence that most of the olefin was not formed by a combination reaction between methyl and propenyl radicals.

(b) From the yields of $CH_3CH{=}CHCH_3$, $CH_4$, $C_2H_6$ and $CD_3CH_3$ it is clear that substantial quantities of $CH_3$ radicals must have been generated during run 2. Reactions 2 and 3 followed by the displacement process (1), provide a source of $CH_3$ radicals and serve to explain the yield of non-deuterated 2-butene. Furthermore, since acetyl radicals decompose rapidly at temperatures above 120°, reactions 2 and 3 provide a means for CO production by secondary reactions. This additional source of CO is necessary to account for the fact that the over-all quantum yield of CO is virtually

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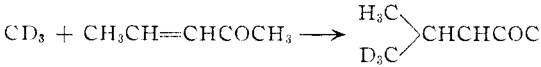
(5) W. A. Noyes, Jr., and L. M. Dorfman, *J. Chem. Phys.*, **16**, 788 (1948).

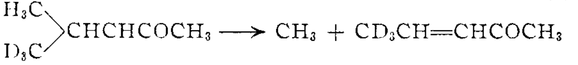
(6) J. R. McNesby and A. S. Gordon, THIS JOURNAL, **76**, 1416 (1954).

unity for the mixture, yet the *trans*-methyl propenyl ketone, which is quite stable compared to acetone, absorbs about one third of the incident 2654–2537 Å. radiation.

Reactions 9 and 10 furnish an alternate method for producing $CH_3$ radicals in run 2. Although there is no direct evidence for this sequence, it may be significant, particularly at high temperatures.



$$CD_3 + CH_3CH{=}CHCOCH_3 \longrightarrow (H_3C)(D_3C)CHCHCOCH_3 \quad (9)$$



$$(H_3C)(D_3C)CHCHCOCH_3 \longrightarrow CH_3 + CD_3CH{=}CHCOCH_3 \quad (10)$$

(c) The fact that all the methane formed was either $CD_3H$ or $CH_4$ demonstrates that only methyl propenyl ketone was the substrate for H atom abstraction by $CH_3$ or $CD_3$ radicals. This seems reasonable since the activation energy for abstraction of an H atom from methyl propenyl ketone should be appreciably less than that for abstraction of a D atom from perdeuteroacetone. In addition to a lower activation energy for $CD_3$ attack on a C–H bond *vs.* a comparable C–D bond, abstraction of a $\gamma$-hydrogen of the unsaturated ketone is favored by the formation of a strongly resonance-stabilized radical as a product.

In agreement with previous work,[3] an actual increase in the fraction of light absorbed at 2654–2537 Å. was observed during the course of each photolysis. This suggests that saturated ketones are products. Evidence available to date[3,7] indicates that one of these is $CH_3CH(CD_3)CH_2COCH_3$. This could be formed by $\beta$-addition of a $CD_3$ radical to the unsaturated ketone to give $CH_3CH(CD_3)CHCOCH_3$ which in turn could abstract a $\gamma$-hydrogen from the substrate to give the final product. Further discussion of this phase of the reaction mechanism must be deferred until more detailed analyses of the condensable fractions are available.

**Crotonaldehyde.**—Blacet and Roof have shown[8] that crotonaldehyde is unusually stable toward photo-dissociation at room temperature and wave lengths from 3130 to 2380 Å. Subsequently, Blacet and LuValle[9] found that at elevated temperatures this aldehyde is still stable at 3130 Å. but that at 2380 Å. and 265° the quantum yield of carbon monoxide is about unity. Among the hydrocarbon products, chiefly propylene, they found small amounts of methane. Recently in a brief investigation Tolberg and Pitts[7] carried out two photolyses of crotonaldehyde at 265° and 2380 Å. Mass spectrometric analysis of the non-condensables confirmed the presence of methane and showed that 2-butene was another "minor" product. They suggested that the 2-butene might be formed by a methyl radical displacement of formyl radical, reaction 11, which would be analogous to the displacement of acetyl by methyl, reaction 1.

$$CH_3 + CH_3CH{=}CHCHO \longrightarrow CH_3CH{=}CHCH_3 + HCO \quad (11)$$

The results of this research confirm the existence of (11) as a secondary reaction of significance in systems containing methyl radicals and crotonaldehyde. The following evidence is offered in support of this statement.

(a) It is evident from the results in Table II that at 170° 2-butene is the major olefin product of photolyses of crotonaldehyde–acetone mixtures at 2654–2537 Å. Its quantum yield increases almost linearly from 0.14 at 170° to about $0.4_5$ at 350°. It seems most unlikely that such substantial yields of 2-butene could arise chiefly from the combination reaction between $CH_3$ and $CH_3CH{=}CH$ radicals, in systems containing a free radical "trap" such as crotonaldehyde. The fact that only traces of ethane, presumably formed by a combination reaction between methyl radicals, were found in these photolyses, substantiates this viewpoint.

(b) The $C_4$ olefin formed in the photolysis of a mixture of $CD_3COCD_3$ and crotonaldehyde was solely $CD_3CH{=}CHCH_3$. This is further indication that 2-butene is formed by direct methyl radical attack on crotonaldehyde.

(c) Pyrolysis of a mixture of di-*t*-butyl peroxide and crotonaldehyde at 170° yielded a substantial amount of 2-butene, about 20% in excess of the propylene formed. Thus "hot" methyl radicals from a primary process or photo-excited crotonaldehyde or acetone molecules are not necessary for the displacement reaction 11.

(d) The yields of hydrogen per quantum absorbed *by the crotonaldehyde* are at least three times larger in the photolysis of mixtures than in the photolysis of crotonaldehyde alone.[10] This can be explained by assuming that (11) acts as another source of formyl radicals. Decomposition of these radicals into H atoms and carbon monoxide, followed by an abstraction reaction, could furnish the additional hydrogen found in excess of that observed in direct photolysis.

Analytical techniques were not available to determine directly the stable condensable products resulting from $\beta$-addition of methyl and other radicals. However, the pronounced increase observed in the percentage of light absorbed at 2654–2537 Å. during the course of a run is indirect evidence for the formation of saturated aldehydes, since the latter absorb strongly in that region compared to crotonaldehyde.

In addition to supplying evidence for the displacement process (11), the data in Table II yield other pertinent facts. These include:

(a) Propylene is produced in a chain process (or processes) that is strongly temperature dependent. $\Phi_{C_3H_6}$ is of the order of 0.13 at 170°, 0.69 at 250° and over five at 350°. The ratio (quantum yield of 2-butene)/(quantum yield of propylene) is 1.1 at 170° but drops to less than 0.1 at 350°.

(b) The quantum yield of carbon monoxide exceeds unity at 140° and is about 11 at 350°. In the case of crotonaldehyde alone, under similar conditions, $\Phi_{CO}$ does not exceed unity until 240° and it reaches about five at 350°.[10]

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[7] R. S. Tolberg and J. N. Pitts, Jr., Abstracts Division of Physical and Inorganic Chemistry, American Chemical Society, April, 1955, Cincinnati, Ohio.

[8] F. E. Blacet and J. G. Roof, THIS JOURNAL, **58**, 73 (1936).

[9] F. E. Blacet and J. E. LuValle, *ibid.*, **61**, 273 (1939).

[10] J. N. Pitts, Jr., R. W. Woolfolk and D. D. Thompson, unpublished results, this Laboratory.

Two quite different reaction sequences can be postulated to account for the large yields of propylene and carbon monoxide.

**Chain A.**—This was first proposed by Blacet and LuValle[9] and is analogous to the typical chain decomposition mechanism well established for the aliphatic aldehydes.

$$\mathrm{CH_3 + CH_3CH{=}CHCHO \longrightarrow CH_4 + CH_3CH{=}CHCO} \quad (12)$$

$$\mathrm{CH_3CH{=}CHCO \longrightarrow CH_3CH{=}CH + CO} \quad (13)$$

$$\mathrm{CH_3CH{=}CH + CH_3CH{=}CHCHO \longrightarrow CH_3CH{=}CH_2 + CH_3CH{=}CHCO} \quad (14)$$

**Chain B.**—The chain carrying step is reaction 17, the displacement of a formyl radical by a hydrogen atom. It is analogous to reaction 11, but no unequivocal evidence was obtained for the process and its existence is in no sense established.

$$\mathrm{CH_3 + CH_3CH{=}CHCHO \longrightarrow CH_3CH{=}CHCH_3 + HCO} \quad (15)$$

$$\mathrm{HCO \longrightarrow H + CO} \quad (16)$$

$$\mathrm{H + CH_3CH{=}CHCHO}\begin{cases}\longrightarrow \mathrm{CH_3CH{=}CH_2 + HCO} & (17)\\ \longrightarrow \mathrm{H_2 + CH_3CH{=}CHCO} & (18)\end{cases}$$

Unfortunately, with the existing data it is difficult, if not impossible, to determine which of these two chains is responsible for the large yields of propylene and carbon monoxide. Actually both chain A and chain B may be involved in the over-all mechanism.

One general argument against chain A is the fact that it involves propagation by the abstraction reactions 12 and 14 in a system containing a high concentration of a free radical "trap," the olefinic double bond in crotonaldehyde. This objection is not a factor in chain B where the displacement process 17 is postulated as the propagating step.

Since the temperature dependence of propylene formation parallels that for hydrogen, one might suggest that this is an indication that the rate of decomposition of formyl radicals in (16) controls the rates of formation of both hydrogen and propylene in the parallel reactions 17 and 18. However, another explanation could be that the activation energy $E_{13}$ for the rate-determining step in chain A, the decomposition of the $\mathrm{CH_3CH{=}CHCO}$ radical, is close to $E_{16}$ for the formyl radical, and the parallelism in quantum yields is coincidental.

No deuterated propylene was detected in the propylene from the photolysis of mixtures of perdeuteroacetone and crotonaldehyde. Chain B is in complete accord with this result. However, the evidence still does not eliminate chain A despite the fact that this chain involves an abstraction reaction by $\mathrm{CH_3CH{=}CH}$ radicals. One might presume that in the presence of such a large quantity of $\mathrm{CD_3COCD_3}$ a significant reaction would be

$$\mathrm{CH_3CH{=}CH + CD_3COCD_3 \longrightarrow CH_3CH{=}CHD + CD_3COCD_2} \quad (19)$$

and deuterated propylene would be a product. This reasoning is invalid since the activation energy for (19) is probably at least two or three kilocalories greater than for abstraction of an acyl hydrogen from crotonaldehyde and at 250° the rate of (19) would be negligible compared to reaction 14.

In an attempt to find another displacement process such as (20) which would be similar to reaction 17, some mixtures of acetaldehyde and *trans*-methyl

$$\mathrm{H + CH_3CH{=}CHCOCH_3 \longrightarrow CH_3CH{=}CH_2 + CH_3CO} \quad (20)$$

propenyl ketone were photolyzed at 2654–2537 Å. under conditions similar to those in Table II. In a 7000 sec. run at 250° the yields at S.T.P. of carbon monoxide, methane and 2-butene were 301, 116 and 84 $\mu$l., respectively. The yield of propylene did not exceed 12 $\mu$l. Only a trace of ethane and no hydrogen were detected. While the substantial yield of 2-butene is further confirmatory evidence for reaction 1, the methyl radical displacement, the small yield of propylene indicates that (20) does not occur to a significant extent under these conditions in this system.

**Kinetics of Displacement Processes.**—The rate of formation of 2-butene, $R_{\mathrm{C_4H_8}}$, in the photolysis of mixtures of acetone and methyl propenyl ketone is given by

$$R_{\mathrm{C_4H_8}} = I_{\mathrm{a}}\Phi_{\mathrm{C_4H_8}} = k_1(\mathrm{CH_3})(\mathrm{CH_3CH{=}CHCOCH_3})$$

if one neglects the small amount of butene formed by a combination reaction. By combining this expression with the rate of formation of ethane and the Arrhenius relationship one obtains

$$\log\left[\frac{\Phi_{\mathrm{C_4H_8}}\, I_{\mathrm{a}}{}^{1/2}}{\Phi^{1/2}{}_{\mathrm{C_2H_6}}\cdot(\mathrm{CH_3CH{=}CHCOCH_3})}\right] = -\frac{(E_1 - {}^1/_2E_8)}{2.30RT} + \log\left(\frac{A_1}{A_8{}^{1/2}}\right)$$

A plot of the term on the left *vs.* $1/T$ permits one to evaluate $(E_1 - {}^1/_2E_8)$ and, since $E_8$ is close to zero, the activation energy for the displacement process (1) is obtained. Unfortunately, with the relatively low light intensities and large methyl propenyl ketone pressures used in this research, $\Phi_{\mathrm{C_2H_6}}$ was very small and subject to large errors. Work is now in progress under experimental conditions favoring larger yields of ethane, and it is hoped that $E_1$ can be evaluated. Similar considerations apply to the calculation of $E_{11}$, the methyl displacement reaction with crotonaldehyde.

If one assumes arbitrarily that only reaction 17 in chain B is significant in producing propylene and that hydrogen is formed only by the abstraction reactions 18 and 21

$$\mathrm{H + CH_3COCH_3 \longrightarrow H_2 + CH_2COCH_3} \quad (21)$$

one can obtain the expression

$$\Phi_{\mathrm{C_3H_6}}/\Phi_{\mathrm{H_2}} = k_{17}/[k_{18} + k_{21}(\mathrm{A})/(\mathrm{C})]$$

where (C) and (A) are the concentrations of crotonaldehyde and acetone, respectively. In the runs in Table II the ratios (A)/(C) are close to unity, and if one assumes that $k_{21} << k_{18}$ the expression reduces to

$$\Phi_{\mathrm{C_3H_6}}/\Phi_{\mathrm{H_2}} = k_{17}/k_{18}$$

From the slope of a plot of log $[\Phi_{\mathrm{C_3H_6}}/\Phi_{\mathrm{H_2}}]$ *vs.* $1/T$ for data at 210° and above, $(E_{17} - E_{18})$ was estimated to be about −0.5 kcal. There was considerable scatter to the points due to the small yields of hydrogen and the large dark corrections at 350°, but *if* the original assumptions are valid this result indicates that the activation energy for the H atom displacement process is about equal to or slightly less than that of the H atom abstraction from crotonaldehyde. The value for the latter reaction is not known, but the similar reaction with acetaldehyde is reported to have an activation energy $\leq$ 6 kcal.[11] If, of course, chain A supplies a significant amount of propylene the kinetics become more complex and this treatment breaks down.

## Summary

It now seems well established that displacement processes are important modes of reaction of methyl radicals with biacetyl,[12] *trans*-methyl propenyl ketone and crotonaldehyde. Recently other displacement processes have been reported to occur when methyl radicals react with propylene and 1-butene. Varnerin[13] states that at least 5% of the methyl radicals generated in the pyrrolysis of mixtures of $CD_3CDO$ and propylene react by (22)

$$CD_3 + CH_2{=}CHCH_3 \longrightarrow CD_3CH{=}CH_2 + CH_3 \quad (22)$$

McNesby and Gordon photolyzed acetone-$d_6$ in the presence of 1-butene[14] at 375 and 500° and explain their results by a mechanism which includes the displacement process

$$CD_3 + CH_2{=}CHCH_2CH_3 \left\{ \begin{array}{l} \longrightarrow CD_3CH_2CH{=}CH_2 + CH_3 \\ \longrightarrow CH_2{=}CHCD_3 + C_2H_5 \end{array} \right.$$

Within a few weeks the reverse reactions were reported by Kebarle and Bryce.[15] In both instances

$$CH_3 + CH_2{=}CHCH_2CD_3 \left\{ \begin{array}{l} \longrightarrow CH_3CH_2CH{=}CH_2 + CD_3 \\ \longrightarrow CH_2{=}CHCH_3 + CH_2CD_3 \end{array} \right.$$

the investigators propose that methyl radicals first add to the double bond to form an intermediate radical which subsequently dissociates into a new olefin and another free radical. For example, McNesby and Gordon visualize the two step process

$$CD_3 + CH_2{=}CHCH_2CH_3 \longrightarrow [CD_3CH_2CHCH_2CH_3]$$
$$[CD_3CH_2CHCH_2CH_3] \longrightarrow CD_3CH_2CH{=}CH_2 + CH_3$$

A similar intermediate has been suggested in the methyl displacement of acetyl from methyl propenyl ketone[3] and may exist in the analogous process with crotonaldehyde. However, there is little if any direct evidence for these intermediates.

An interesting process, recently suggested by Kistiakowsky and Mahan[16] to explain their results from the photolysis of methyl ketene, is the attack of the ethylidene radical on methyl ketene to give butene and CO

$$CH_3CH + CH_3CH{=}C{=}O \longrightarrow C_4H_8 + CO$$

This process can be classified as a displacement of carbon monoxide by the ethylidene radical.

Two examples of what might be termed H atom displacements are proposed by Rabinovitch, Davis

$$H + CH_3CH{=}CH_2 \longrightarrow CH_2{=}CH_2 + CH_3$$

and Winkler[17] and reported by Forst and Winkler.[18]

$$H + CH_3CN \longrightarrow HCN + CH_3$$

The recent accumulation of this body of evidence for free radical displacement processes indicates that secondary reactions of this type may be of considerable importance in a number of other systems similar to those described. Current studies in this Laboratory include an investigation of the reactions of methyl radicals with the $\alpha,\beta$-unsaturated ester, methyl crotonate.

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# Ultrasonic Interferometer Measurements of the Amount of Bound Water. Saccharides

BY HAZIME SHIIO

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Ultrasonic velocities in aqueous solutions of a number of saccharides have been measured with an ultrasonic interferometer, and the amounts of hydration have been determined at 25°. The following samples were studied: xylose, arabinose, fructose, glucose, $\alpha$-methyl glucoside, sucrose, maltose, cellobiose and raffinose. The amount of bound water obtained is 0.28, 0.42, 0.38, 0.35, 0.23, 0.20, 0.22, 0.25 and 0.22 cc./g. solute, respectively. From these values, it is shown that 0.5–0.9 water molecules are hydrated to one OH radical of each saccharide. Further investigations were carried out on the hydrations of a few saccharides at various temperatures, and the enthalpy difference between hydrate water and non-hydrated has been estimated to be about 12–13 kcal./mole.

## Introduction

The compressibility of the solution may be determined by the effects from solvent, solute and solvation. The effects of the solute are separated into two parts: the compressibility of the solute molecule and solute–solute interaction. If the concentration of the solution becomes sufficiently low, the second effect becomes negligible. The