[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF NORTHWESTERN UNIVERSITY]

# A Vapor-phase Free Radical Displacement Reaction: the Reaction of Methyl Radicals with *trans*-Methyl Propenyl Ketone[1]

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

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Methyl radicals from the photolysis of acetone or the pyrolysis of di-*t*-butyl peroxide react with *trans*-methyl propenyl ketone by the free radical displacement process $CH_3 + CH_3CH{=}CHCOCH_3 \rightarrow CH_3CH{=}CHCH_3 + CH_3CO$. At 150° the acetyl radical dissociates into $CH_3 + CO$, resulting in a chain of short length. It is proposed that the primary step is the $\alpha$-addition of $CH_3$ to the ketone to give the unstable intermediate $CH_3CHCH(CH_3)COCH_3$ which decomposes into 2-butene and acetyl. Beta addition of $CH_3$ leads to condensable products, one of which appears to be $(CH_3)_2CHCH_2COCH_3$. Methyl radicals were shown to react with $(CH_3)_2CHCH_2COCH_3$ at 150° to give isobutylene and CO in equal yields. A mechanism for this process is proposed.

Usually vapor-phase free radical reactions are classified as abstraction, disproportionation, recombination, addition or decomposition. Recently good evidence for another type of free radical process has been obtained by Blacet and Bell[3] and by these investigators.[1] Both cases involved attack of methyl radicals on the $\alpha,\beta$-unsaturated ketones, biacetyl[3] and *trans*-methyl propenyl ketone.[1]

A novel feature in the photolyses of biacetyl was the large yields of acetone, apparently as a result of a chain process. The following sequence of reactions was postulated by Blacet and Bell to account for this observation

$$CH_3 + CH_3COCOCH_3 \longrightarrow CH_3COCH_3 + CH_3CO \quad (1)$$

$$CH_3CO \longrightarrow CH_3 + CO \quad (2)$$

They calculated the rate constant of (1) to be $k = 10^{10.7}\exp(-5000/RT)$ moles/cc. sec.

Results for the reaction of methyl radicals with *trans*-methyl propenyl ketone have been described briefly in a Communication.[1] In this paper they will be presented in detail and subsequent data of significance also will be given.

## Experimental

The apparatus, analytical techniques and photochemical procedures employed were similar to those described in a previous paper.[4]

**Apparatus.**—All photolyses and pyrolyses, with the exception of one series of runs, were carried out in the same reaction system. The cylindrical reaction cell was fused quartz, 20.0 cm. long, 30.0 mm. i.d.; it had a volume of 140 cc. The cell, set in an aluminum block oven, was filled almost completely with a parallel beam of radiation arising from a Type A Hanovia quartz-mercury arc followed by a Farrand Model 300 U V monochromator. The fraction of light transmitted was measured with an RCA 935 phototube, while absolute intensities were determined 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 *trans*-crotonyl chloride. The crude material was purified by distillation through a small Vigreux column and the fraction boiling at 120–121° was collected. This fraction was redistilled through a Piros–Glover spinning band column at a reflux ratio of 20:1, and the product boiling at 121.1° retained. This fraction, $n^{20}D$ 1.4357, was distilled *in vacuo* into the ketone reservoir and stored at −79°. A highly purified sample of di-*t*-butyl peroxide was kindly supplied by Dr. F. Seubold. Mallinckrodt "Analytical Grade" acetone was distilled *in vacuo* into the actinometer reservoir. The quantum yield of carbon monoxide from acetone was assumed to be 1.00 at 120° and above.

*Analytical Methods.*—Photolyses were run less than 5% toward completion to prevent undesirable side reactions. Pyrolyses were made in the dark with approximately 1:5 mixtures of di-*t*-butyl peroxide and *trans*-methyl propenyl ketone, respectively. Runs were timed to last three to four half-lives of the peroxide. Two modified Le Roy stills[5] were used in series to separate several cuts of the gaseous products from the condensate. A portion of the $C_1$ cut was analyzed for carbon monoxide with a Blacet–Leighton apparatus. The remainder of the $C_1$ cut and the $C_2 + C_3$ and $C_4$ fractions were analyzed with the aid of a Westinghouse Type LV mass spectrometer.

In order to collect a sample of butene large enough for quantitative infrared analysis, a series of five pyrolyses of the di-*t*-butyl peroxide and methyl propenyl ketone mixtures were carried out at 170° in a one-liter Pyrex reaction chamber. From the total non-condensables at −79° for each run, the $C_4$ fraction was separated by means of a Le Roy still; then the five successive butene samples were combined and transferred to a gas cell for analysis. It was necessary to employ infrared analysis because the similarity of the mass spectra of the isomeric butenes made it impossible to analyze them accurately with the mass spectrometer.

## Results

**Photolysis of *trans*-Methyl Propenyl Ketone at 2380 Å.**—Although the photochemistry of this ketone has been presented[6] in detail, certain of the results furnish direct evidence for the displacement process under consideration, and they are therefore summarized below.

The major hydrocarbon product, of those identified, from all direct photolyses of *trans*-methyl propenyl ketone at 2380 Å. and various temperatures, pressures and intensities was 2-butene. For example, at 275° and 5 mm. pressure the quantum yield of 2-butene was 0.32 compared to 0.22, 0.13, 0.010 and 1.15 for the quantum yields of methane, propylene, ethane and carbon monoxide, respectively.

**Photolysis of a *trans*-Methyl Propenyl Ketone–Acetone Mixture at 2654 Å.**—A mixture of acetone, as a methyl radical source, and *trans*-methyl propenyl ketone was photolyzed at 2654 Å. and 275°. This wave length was selected since it falls near the maximum in the first absorption band for

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(1) Presented in part at the conference on Photochemistry and Free Radicals, University of Rochester, September, 1954; also in a "Communication to the Editor," J. N. Pitts, Jr., R. S. Tolberg and T. W. Martin, THIS JOURNAL, **76**, 2843 (1954). Abstracted in part from the Ph.D. theses submitted to Northwestern University by R. S. Tolberg who held an Atomic Energy Commission predoctoral fellowship during 1951–1953, and T. W. Martin who held a U. S. Rubber Company Fellowship.

(2) Division of Physical Sciences, University of California, Riverside, California; address to which communications should be sent.

(3) F. E. Blacet and W. E. Bell, *Disc. Faraday Soc.*, **14**, 70 (1953).

(4) T. W. Martin and J. N. Pitts, Jr., THIS JOURNAL, **77**, 5465 (1955).

(5) D. J. Le Roy, *Can. J. Research*, **B28**, 492 (1950).

(6) R. S. Tolberg and J. N. Pitts, Jr., THIS JOURNAL, in press.

acetone, and in the minimum between the first two absorption bands of methyl propenyl ketone. Photolyses also were carried out under similar conditions for the two pure ketones. Results for the three runs are given in Table I.

**Pyrolyses of Mixtures of *trans*-Methyl Propenyl Ketone and Di-*t*-butyl Peroxide.**—Several mixtures of the peroxide and the ketone were heated in the dark at 170 and 150° for several half-lives of the peroxide. Under these conditions the peroxide is an excellent source of methyl radicals.[7] Results from these pyrolyses are given in Table II. No propylene was detected in these runs.

TABLE I

RATE OF FORMATION OF GASEOUS PRODUCTS FROM THE PHOTOLYSIS OF ACETONE, METHYL PROPENYL KETONE (MPK) AND A MIXTURE OF THE TWO KETONES AT 2654 Å. AND 275°

| Ketone | Acetone | MPK | Acetone + MPK |
|---|---|---|---|
| Pressure, mm. | 33.0 | 41.5 | 42.0 MPK<br>33.0 Acetone |
| Fraction light absorbed, $Q_m$ | | | |
| Start | $0.42_5$ | $0.21_5$ | 0.58 |
| Finish | $0.41_5$ | $0.33_0$ | 0.78 |
| Calcd. (time av.), $Q_m$ | 0.42 | 0.28 | 0.64 |
| $I_a$, (quanta abs./sec.) $\times 10^{-14}$ | 2.07 | 1.29 | 3.26 |
| Time, sec. $\times 10^{-4}$ | 0.750 | 2.18 | 2.17 |
| Quantum yield CO | 1.00[a] | 0.50 | 1.43 |
| (Molecules product/sec.) $\times 10^{-14}$ | | | |
| CO | 2.10 | 0.64 | $4.6_8$ |
| 2-Butene | .. | $.18_8$ | 1.39 |
| Propylene | .. | $.05_4$ | 0.21 |
| Methane | 3.05 | $.10_8$ | 1.28 |
| Ethane | $0.09_1$ | $.001_9$ | 0.010 |

[a] Assumed to be unity.

The infrared analysis of the total butenes from the five successive pyrolyses at 170° described under Analytical Methods gave 32.6% *cis*-2-butene, 22.2% isobutylene and by difference 45.2% *trans*-2-butene.

**Pyrolysis of a Mixture of Di-*t*-butyl Peroxide and Methyl Isobutyl Ketone.**—Methyl isobutyl ketone has been identified as a product of the photolysis of *trans*-methyl propenyl ketone.[6] In the present work, the conditions under which the series of pyrolyses were carried out in the one liter reaction chamber were particularly favorable for the formation of this saturated ketone. Thus, to check on possible side reactions of methyl radicals with this ketone, a mixture of 77 mm. of methyl isobutyl ketone and 16 mm. of di-*t*-butyl peroxide were pyrolyzed at 150° for four hours. The volumes of the major non-condensable products (microliters at 25° and 750 mm.) were : ($CH_4$ + $C_2H_6$) = 1981, CO = 203 and isobutylene = 206. Peaks, probably due to traces of pentene, neohexane and isopentane, also were found in the mass spectrum of the products.

## Discussion

The following sequence of reactions will account for the large yields of 2-butene observed when methyl radicals are reacting with *trans*-methyl propenyl ketone

$$CH_3CH{=}CHCOCH_3 + CH_3 \longrightarrow CH_3CH{=}CHCH_3 + CH_3CO \quad (3)$$

$$CH_3CO \longrightarrow CH_3 + CO \quad (2)$$

Experimental evidence supporting this mechanism is cited in the following discussion.

The sequence (3), (2) has chain properties. This would account for the fact that the quantum yield of carbon monoxide exceeds unity in the photolysis of pure *trans*-methyl propenyl ketone at 2380 Å. and 275°.[6] The reactions also serve to explain the quantum yield of carbon monoxide of 1.43 obtained in the photolysis of a mixture of acetone and methyl propenyl ketone at 2654 Å. and 275°. Under these conditions, the quantum yields of carbon monoxide in photolyses of the pure ketones are 1.00 and 0.50, respectively, and if no chain occurred, $\Phi_{CO}$ in the mixture would be expected to fall somewhere between these values. More conclusive evidence for the sequence (3), (2) is the fact that in the photolysis of the mixture, seven times as much 2-butene was formed as in the photolysis of the pure ketone.

TABLE II

VOLUMES OF NON-CONDENSABLE PRODUCTS[a] FROM PYROLYSES OF DI-*t*-BUTYL PEROXIDE AND *trans*-METHYL PROPENYL KETONE MIXTURES

| | CO | $C_4H_8$[b] | $CH_4$ | $C_2H_6$ |
|---|---|---|---|---|
| [Peroxide (17 mm.) + ketone (79 mm.)] at 170° for 22 min. | 257 | 248 | 291 | 408 |
| [Peroxide (18 mm.) + ketone (86 mm.)] at 150° for 183 min. | 256 | 264 | 423 | 107 |
| [Peroxide (17 mm.) + ketone (83 mm.)] at 150° for 200 min. | 313 | 374 | 475 | 176 |

[a] Values given are volumes of products in microliters (25° and 750 mm. pressure). [b] Total 2-butene based on mass 56 peak.

From the data in Table II, it is evident that reaction 3 does not require "hot" methyl radicals generated by photolytic methods. The process is also efficient with methyl radicals produced by thermal means at 150 and 170°. The equivalence, within experimental error, of the yields of carbon monoxide and 2-butene at temperatures where *trans*-methyl propenyl ketone is stable is excellent confirmatory evidence that these products are generated in the same reaction sequence.

Both *trans*- and *cis*-2-butene were products, their ratio being about 1.4:1, respectively, in the $C_4$ fraction collected from the series of pyrolyses at 170°. The fact that a mixture of *trans* and *cis* isomers is obtained suggests that they are each formed through an intermediate radical as shown in reactions 4 and 5. Since (4) is probably not a reversible process, there is no reason to presume that the 2-butene product should be the 2:1 mixture of *trans* and *cis* forms in thermodynamic equilibrium at 170°. It is more probable that the dis-

$$CH_3 + CH_3CH{=}CHCOCH_3\ (trans) \longrightarrow [CH_3CHCH(CH_3)COCH_3]^* \quad (4)$$

$$[CH_3CHCH(CH_3)COCH_3]^* \longrightarrow CH_3CH{=}CHCH_3\ (\text{mixture}) + CH_3CO \quad (5)$$

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[7] J. H. Raley, F. F. Rust and W. E. Vaughan, THIS JOURNAL, **70**, 88, 1336, 2767 (1948).

sociation of the postulated intermediate is kinetically controlled and that a difference in activation energy favors the formation of the *trans* isomer in step (5). Actually, an argument based on this limited evidence is not conclusive because there is some chance that a substantial portion of the *trans*-methyl propenyl ketone may have undergone a radical induced isomerization to the *cis* form prior to the displacement of acetyl by methyl.

Reaction 3 is similar in principle to that reported by Rabinovitch, Davis and Winkler[8,9] for the reaction of H atoms with propylene (6). They regard (6) as proceeding through the vibrationally excited

$$H + CH_3CH{=}CH_2 \longrightarrow CH_2{=}CH_2 + CH_3 \quad (6)$$

intermediate $[CH_2CH_2CH_2]^*$, rather than occurring as a one-step process. This mechanism would be analogous to the consecutive reactions 4 and 5.

By analogy with the terminology employed for a number of ionic reactions in solution reaction 3 can be classified as a displacement of acetyl radical by methyl radical. This term was also used by Blacet and Bell to describe reaction 1, the displacement of acetyl by methyl in biacetyl photolysis.[3] However, Trotman-Dickenson prefers to use the term "free radical inversion" to describe 3.[10] In any event, irrespective of the nomenclature employed, reaction 3 seems to represent another type of free radical process of some degree of generality.

**Reactions of Methyl Radicals with Methyl Isobutyl Ketone.**—It can be shown from a material balance that a large percentage of the methyl radicals generated in these studies must add to the β-carbon of *trans*-methyl propenyl ketone. Presumably, the relatively stable allylic radical formed, $(CH_3)_2CHCHCOCH_3$, can then abstract a hydrogen atom (probably from the active γ-hydrogens of the methyl propenyl ketone substrate) to form methyl isobutyl ketone, or it can combine with other radicals, or dissociate. In the latter case, dissociation back into methyl radicals and methyl propenyl ketone seems most likely. Qualitative mass spectrometric evidence for an ultimate product of β-addition, methyl isobutyl ketone, has been reported.[6] Further evidence for the formation of saturated ketones in the present research is the observation that the fraction of light absorbed at 2654 Å., $Q_m$, increased during the photolysis of mixtures of methyl propenyl ketone and acetone (see Table I). This is reasonable since 2654 Å. is near a maximum of absorption for saturated ketones and a minimum for the α,β-unsaturated ketones. Each acetone molecule gives two methyl radicals on photodecomposition at 275°, and if this effect alone were operative, the fraction of light absorbed would decrease. However, if more than half of these methyls add β and ultimately lead to saturated branched ketones as products, the over-all effect would be the observed increase in $Q_m$.

Isobutylene accounted for more than 20% of the butenes collected for infrared analysis in the series of pyrolyses of di-*t*-butyl peroxide and methyl propenyl ketone mixtures. If one assumes that methyl isobutyl ketone accumulated in the pyrolysis vessel because of reactions 7 and 8 and was present in appreciable amounts during the later runs in the series, the following sequence of reactions offers an attractive explanation for the large yield of isobutylene when none was detected by suitable mass spectral peak ratios in the individual runs reported in Table II

$$CH_3CH{=}CHCOCH_3 + CH_3 \longrightarrow (CH_3)_2CHCHCOCH_3 \quad (7)$$

$$(CH_3)_2CHCHCOCH_3 + CH_3CH{=}CHCOCH_3 \longrightarrow (CH_3)_2CHCH_2COCH_3 + CH_2CH{=}CHCOCH_3 \quad (8)$$

$$(CH_3)_2CHCH_2COCH_3 + CH_3 \longrightarrow (CH_3)_2CCH_2COCH_3 + CH_4 \quad (9)$$

$$(CH_3)_2CCH_2COCH_3 \longrightarrow (CH_3)_2C{=}CH_2 + COCH_3 \quad (10)$$

$$COCH_3 \longrightarrow CO + CH_3 \quad (2)$$

Reactions 8 and 9 were tested directly by pyrolyzing a mixture of methyl isobutyl ketone and di-*t*-butyl peroxide. In accord with the postulated mechanism, carbon monoxide and isobutylene were formed in appreciable and equal yields. Thus, while the data on this type of process are limited, it is of significance in certain systems and warrants further investigation.

In order to test further the mechanisms proposed in this paper, studies are in progress in which $CD_3$ and other radicals are generated in the presence of methyl propenyl ketone, crotonaldehyde and related α,β-conjugated compounds. Results to date[11] are in accord with the displacement type of mechanism presented in this paper.

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EVANSTON, ILLINOIS

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[9] B. S. Rabinovitch, S. G. Davis and C. A. Winkler, *Can. J. Res.*, **B21**, 251 (1943).

[10] A. B. Trotman-Dickenson, "Gas Kinetics," Butterworth Scientific Publications London, 1955.

[11] J. N. Pitts, Jr., D. D. Thompson and R. W. Woolfolk, THIS JOURNAL, in press.