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given concentration is approximately the same as for the thermal diffusion column.

The two-phase counter-current exchange methods developed by Urey and his co-workers[1] have been used to produce concentrations as high as 25 percent C^{13} at high transport rates of 2×10^{-6} g/sec. of C^{13}. The power requirements with these methods are low; they are therefore much more economical.

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The Mercury Photosensitized Hydrogenation of Propylene*

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The mercury photosensitized hydrogenation of propylene has been investigated at 30°, 110°, and 200°, using an 8/1 ratio of hydrogen to propylene. The hydrocarbon products were analyzed with a mass spectrometer. The occurrence of 2,3-dimethylbutane as the principal C_6 product indicates that a hydrogen atom adds preferentially to the terminal carbon atom of propylene to form the isopropyl radical. Analyses of the C_6 and C_9 products suggests that the isopropyl radical adds preferentially to the middle carbon atom of propylene.

A CONVENIENT source of hydrogen atoms in low concentrations is provided by the reaction of excited mercury atoms with molecular hydrogen:

$$\mathrm{Hg}({}^1S_0)+h\nu(2537\text{ A.U.})=\mathrm{Hg}({}^3P_1)$$
$$\mathrm{Hg}({}^3P_1)+\mathrm{H}_2=\mathrm{Hg}({}^1S_0)+2\mathrm{H}.$$

If hydrogen atoms are produced in this way in a mixture of hydrogen and an olefin, the subsequent addition of a hydrogen atom to the olefinic double bond will yield an aliphatic free radical. For example:

$$\mathrm{H}+\mathrm{C_2H_4}=\mathrm{C_2H_5}.$$

The reaction products from the mercury photosensitized hydrogenation at 25°C of ethylene, propylene, and butene-2 were analyzed by Moore and Taylor,[1] who found a considerable formation of the radical recombination products, butane, hexane, and octane, respectively. Thus,

$$2\mathrm{C_2H_5}=\mathrm{C_4H_{10}};\quad 2\mathrm{C_3H_7}=\mathrm{C_6H_{14}};\quad 2\mathrm{C_4H_9}=\mathrm{C_8H_{18}}.$$

These reactions were carried out with a high (about 8 to 1) ratio of hydrogen to olefin. This has the effect of minimizing photosensitized reactions of the olefins themselves, which might otherwise obscure the simple atomic hydrogen reactions. The quenching cross section of propylene is probably around ten times[2] that of hydrogen for $\mathrm{Hg}({}^3P_1)$. In the absence of hydrogen excited ethylene or propylene molecules are readily deactivated without undergoing chemical reaction.[3] It is probable, however, that some formation of hydrogen atoms and propyl radicals occurs through the reaction of excited propylene with molecular hydrogen:

$$\mathrm{C_3H_6}^*+\mathrm{H_2}=\mathrm{C_3H_7}+\mathrm{H}.$$

The quenching cross sections of the saturated hydrocarbons are much lower than those of the olefins. With the excess of hydrogen used it is therefore possible to study the hydrogenation reactions of the olefins without undue complications from the mercury photosensitized reactions of the hydrocarbon reactants and products.

The present work is a more extended investigation of the mercury photosensitized hydrogenation of propylene over a range of tempera-

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[1] W. J. Moore and H. S. Taylor, J. Chem. Phys. 8, 504 (1940).

[2] K. J. Laidler, J. Chem. Phys. 15, 718 (1947).

[3] H. E. Gunning and E. W. R. Steacie, J. Chem. Phys. 14, 57 (1946).

tures from 30° to 200°. The reaction products were analyzed by means of a mass spectrometer, so that the isomeric hydrocarbons could be identified precisely even with samples amounting to around 10 cc of vapor.

EXPERIMENTAL

Purified hydrogen and propylene were introduced into a cylindrical quartz reaction vessel, 40 mm in diameter and 40 cm long. Mercury vapor was provided by a pool of mercury maintained at 25°C in a short length of tubing at the bottom of the reaction vessel. The vessel was surrounded by a furnace, except for a narrow slit into which was fitted the ultraviolet lamp, a Hanovia SC-2537 mercury-resonance discharge tube providing an intense source of 2537 A.U. resonance radiation. Temperature was measured by means of a thermometer suspended inside the reaction vessel.

When the arc was turned on the photosensitized reaction proceeded very rapidly; it was followed by the accompanying fall in pressure. In a typical run at 30°C with 32 mm propylene and 249 mm hydrogen, the pressure fall amounted to a practically linear drop of 18 mm in 8 minutes, after which time there was no further decline in pressure. The arc was turned off about two minutes after the pressure fall ceased.

Then the products condensable at liquid nitrogen temperature (−195°C) were frozen out by repeated passage of the product gases back and forth through a chilled trap. The non-condensable gases, presumed to be almost entirely methane and residual hydrogen, were withdrawn with a Töpler pump. The hydrogen was burned on cupric oxide at 300°C, the water vapor condensed in a −78°C cold trap, and the residual gas recorded as methane. The fraction condensed at −195°C was analyzed by means of a Consolidated mass spectrometer. These analyses were provided through the kind cooperation of the mass spectrometer section of the National Bureau of Standards.

EXPERIMENTAL RESULTS

The course of the pressure-time curves is illustrated by the examples in Fig. 1. Not much kinetic information can be derived from these curves. They appear to indicate a constant reaction rate determined solely by the rate of production of hydrogen atoms.

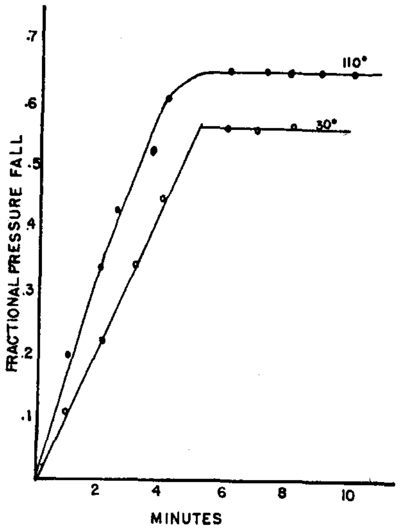


FIG. 1. Pressure-time curve.

It was found that some of the propylene remained unreacted at the end of the run, and the analytical results have been calculated on the basis of the portion of propylene that was consumed. These analyses are summarized in Table I.

It was not possible to identify exactly the nonane found. Mass spectrometer patterns for 15 out of the total of 35 different nonanes were compared with the unknowns. This inability to identify the C_9 component introduces a small uncertainty into the reported analyses, perhaps of the order of ±1 percent.

CONCLUSIONS AND DISCUSSION

A. The Addition of Hydrogen Atoms to Propylene

It is evident that, except for a trace of 2,2-dimethyl-butane, the only hexane formed in these reactions is 2,3-dimethylbutane (di-isopropyl). This fact leads to the conclusion that when a hydrogen atom adds to propylene it does so exclusively at the terminal carbon atom, yielding the isopropyl radical:

$$H+CH_3—CH=CH_2 = CH_3—CH—CH_3. \quad (1)$$

The addition to the middle carbon atom does not occur:

$$H+CH_3—CH=CH_2 = CH_3\cdot CH_2\cdot CH_2. \quad (2)$$

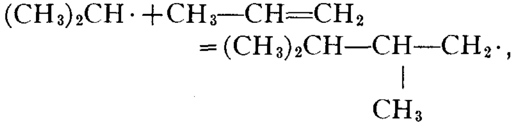
TABLE I. Products from mercury photosensitized hydrogenation of propylene with 8:1 hydrogen/propylene ratio.

Run No. Temperature, °C	1 30	2 30	3 110	4 200
Methane	6	6	17	32
Ethane	4	2	2	5
Propane	46	55	40	28
n-Butane	4	4	3	4
Butenes	2	0	4	5
Pentanes	1	1	3	6
2,3-Dimethylbutane	35	30	27	13
2,2-Dimethylbutane	1	—	1	1
Nonane	2	1	1	3

Two isopropyl radicals may then recombine to yield 2,3-dimethylbutane:

$$2(CH_3)_2CH\cdot = (CH_3)_2CH—CH(CH_3)_2. \quad (3)$$

An alternative mechanism for the formation of hexane is the addition of an isopropyl radical to propylene, followed by addition of a hydrogen atom to the hexyl radical so formed.



$$(CH_3)_2CH\cdot + CH_3—CH{=}CH_2 = (CH_3)_2CH—\underset{CH_3}{\underset{|}{CH}}—CH_2\cdot, \quad (4)$$

$$(+H) = (CH_3)_2CH—CH(CH_3)_2. \quad (5)$$

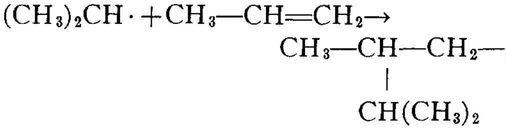
The product of these steps is again 2,3-dimethylbutane.

The failure to obtain any evidence for the occurrence of a normal propyl radical probably is due to a difference in the activation energies, $E_2 - E_1$, for the addition of a hydrogen atom to the middle and the terminal carbon in propylene, since there is little reason to suppose that there is any considerable activation entropy difference. An estimate of the minimum value of $E_2 - E_1$ can be obtained from the analytical data. Let us assume that at 110°, at which temperature 2,3-dimethyl butane constituted 27 percent of the products, not more than 1 percent of 2-methylpentane was formed. This is approximately equivalent to assuming that the rate of reaction (1) is 27 times that of reaction (2). It then follows that $E_2 - E_1 = \Delta E = 2400$ calories.

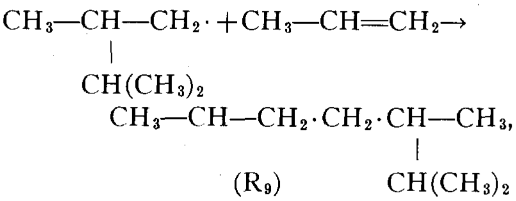
It is interesting to note that Steacie, LeRoy, and Potvin[4] found no evidence for *n*-propyl in the cadmium photosensitized reaction of propane. It therefore appears that both in the addition of a hydrogen atom to propylene and in the removal of a hydrogen atom from propane, the sole product is the isopropyl radical, at least at temperatures up to around 300°C.

B. Polymerization Reactions: The Addition of Isopropyl to Propylene

The occurrence of nonane among the reaction products can be explained by a polymerization process initiated by the addition of isopropyl to propylene. The following reaction sequence may be postulated:



$$(CH_3)_2CH\cdot + CH_3—CH{=}CH_2 \rightarrow CH_3—\underset{CH(CH_3)_2}{\underset{|}{CH}}—CH_2—, \quad (6)$$



$$CH_3—\underset{CH(CH_3)_2}{\underset{|}{CH}}—CH_2\cdot + CH_3—CH{=}CH_2 \rightarrow \underset{(R_9)}{CH_3—CH—CH_2\cdot CH_2\cdot}\underset{CH(CH_3)_2}{\underset{|}{CH}}—CH_3, \quad (7)$$

$R_9 + H \rightarrow$ 2,3-dimethylheptane.

If the hexyl radical formed in reaction (6) picked up a hydrogen atom, the product would be 2,3-dimethylbutane, which is the experimentally found hexane. It is expected that this mechanism for its formation would be almost as favorable as that involving the combination of two isopropyl radicals. Reaction (6) indicates that when isopropyl adds to propylene it does so preferentially at the central carbon atom. It therefore differs in this respect from the hydrogen atom which adds only at the terminal carbon atom. If isopropyl added at the terminal carbon, one would expect to find 2-methylpentane among the reaction products, but this is not in fact observed.

It was not possible to identify the nonane formed, for out of the 35 possible isomeric nonanes, only 15 were available as pure samples for matching the mass spectrometer patterns. Most of these 15 were highly branched isomers. Unfortunately 2,3-dimethylheptane was not available. The nonane 2,3,5-trimethylhexane was among those tested and its absence was indicated. This lends further support to the hypothesis that isopropyl adds to the central carbon of propylene, for addition to the terminal carbon fol-

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[4] E. W. R. Steacie, D. J. LeRoy, and R. Potvin, J. Chem. Phys. 9, 306 (1941).

lowed by combination of the hexyl radical so formed with an isopropyl would have yielded 2,3,5-trimethylhexane. More detailed analysis of the free radical polymerization mechanisms should be postponed until additional mass spectrometer data are available, but the possibility of working out definite reaction sequences from the observed isomeric constitution of the products appears quite promising.

C. Cracking Reactions

In this investigation the hydrogen atom concentration was considerably higher than that used in the earlier work of Moore and Taylor,[1] since a greater intensity of ultraviolet radiation was used. Therefore, cracking reactions occurred to a greater extent. This effect of an increased hydrogen atom concentration is shown very clearly in the study by Rabinowitch, Davis, and Winkler[5] of the reaction of propylene with hydrogen atoms produced by the discharge tube method. The products found in this case were methane, ethane, and propane. It is evident that high concentrations of atomic hydrogen favor cracking reactions such as the following:

$$H+C_3H_7=CH_3+C_2H_5. \qquad (8)$$

It is probably less likely that cracking occurs according to:

$$H+C_3H_7=C_2H_4+CH_4. \qquad (9)$$

Once methyl and ethyl radicals are formed, the production of the observed methane, ethane, butane, and pentane is readily explained.

D. The Occurrence of 2,2-Dimethylbutane

The small amount of 2,2-dimethylbutane reported in the analysis is rather difficult to explain. Although other mechanisms might be devised to account for it, the following rather unusual reaction may be possible:

$$2(CH_3)_2CH=(CH_3)_3—C—CH_2—CH_3. \qquad (10)$$

This involves a shift in the methyl group and may proceed through the intermediate formation of the tertiary butyl radical by a methyl-hydrogen atom disproportionation. On the other hand, the 2,2-dimethylbutane may be a secondary product arising from reaction of the primary saturated products with excited mercury, since irradiation was continued for several minutes after the cessation of the hydrogenation reactions. It would be preferable in future work of this kind to stop irradiation the moment the pressure fall ceases.

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[5] B. S. Rabinowitch, S. G. Davis, and C. A. Winkler, Can. J. Research **B21**, 251 (1943).