mechanism should be applicable, namely

$$R_2C = O + HA \xrightarrow{\text{fast}} (R_2COH)^+ + A^- \qquad (10a)$$

$$(R_2COH)^+ + CN^- \xrightarrow{\text{slow}} R_2C(OH)CN \qquad (10b)$$

However, such a mechanism is not compatible with the observed kinetics since the second-order rate constant relative to carbonyl and HCN would be independent of the pH and this is not the case.

In the case of general acid catalysis, if the value of α in the Brönsted catalytic equation is close to zero,[23] general acid catalysis may be obscured since the solvent molecules which are present in large excess may act as an acid. It is possible that this is the case in cyanohydrin formation as evidenced by the fact that a small general catalytic effect existed in the propionaldehyde reaction and none in the other two reactions. Accordingly, there are three possible mechanisms of interest.

$$>C{=}O + H_2O \overset{\text{fast}}{\rightleftarrows} >C{=}O\ldots H_2O \text{ (hydrogen bond)} \qquad (11a)$$

$$>C{=}O\ldots H_2O + CN^- \xrightarrow{\text{slow}} >C(CN)OH + OH^- \qquad (11b)$$

$$>C{=}O + CN^- \overset{\text{fast}}{\rightleftarrows} >C(CN)O^- \qquad (12a)$$

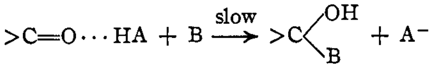
$$>C(CN)O^- + H_2O \xrightarrow{\text{slow}} >C(CN)OH + OH^- \qquad (12b)$$

$$>C{=}O + H_2O + CN^- \xrightarrow{\text{slow}} >C(CN)OH + OH^- \qquad (13)$$

The mechanism 11a, 11b is preferred because: (1) reaction 12b requires that a simple proton transfer to an oxygen atom be rate-determining, whereas experience indicates that such a process is instantaneous; (2) the usual argument against a true termolecular process.

The mechanism represented by (11a, b) is generalized for any carbonyl addition by

$$>C{=}O + HA \overset{\text{fast}}{\rightleftarrows} >C{=}O\cdots HA \qquad (14a)$$



$$>C{=}O\cdots HA + B \xrightarrow{\text{slow}} >C{\begin{smallmatrix}OH\\B\end{smallmatrix}} + A^- \qquad (14b)$$

in which HA is any acid and B is the nucleophilic reagent.

COLLEGE PARK, MD.

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[23] A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," John Wiley and Sons, Inc., New York, N. Y., 1953, p. 219.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CALIFORNIA, DAVIS]

Photochemical Reactions in the Gas Phase Systems: Di-*t*-butyl Peroxide, Peroxide–Butadiene and Acetone–Butadiene

BY DAVID H. VOLMAN AND WENDELL M. GRAVEN[1]

RECEIVED DECEMBER 12, 1952

The absorption spectrum of gaseous di-*t*-butyl peroxide gave no evidence of structure. Combined with photochemical results obtained, this gives evidence for a primary decomposition yield of unity. Methyl and *t*-butoxy radicals from photodecomposing di-*t*-butyl peroxide add to butadiene and initiate polymerization. The activation energy for chain propagation is about 5.8 kcal./mole for peroxide initiation and about 5.0 kcal./mole for acetone initiation. The polymerization rate is linear with butadiene concentration for the peroxide initiation but reaches a maximum and then falls off for the acetone initiation. This is evidence for a photoactivated state and collisional deactivation of acetone molecules. When acetone is photolyzed in the presence of butadiene, ethane is eliminated as a product. Under these conditions butadiene acts as an efficient free radical "trap" for methyl. This shows that ethane cannot be produced by an intramolecular process. A combination of data for the decomposition of the peroxide and acetone in the absence and in the presence of butadiene leads to activation energies of 11.2 ± 2 and 13.5 ± 2 kcal./mole for the decomposition of *t*-butoxy and acetyl radicals, respectively.

Few studies of the photochemistry of dialkyl peroxides are reported in the literature. Prior to the initiation of our experiments, the only work which had come to our attention was a brief report on the photodecomposition products of diethyl peroxide,[2] and a single experiment to determine the decomposition products of liquid di-*t*-butyl peroxide.[3] Results on the photodecomposition of gaseous di-*t*-butyl peroxide[4] appeared while this work was in progress. The results obtained in our study largely substantiate those obtained by Dorfman and Salsburg. However, we have extended the work to include the initiation of chain polymerization of butadiene by radicals from the photolyses of the peroxide and have applied the results to a consideration of the activation energies of *t*-butoxy and acetyl radical decomposition.

Experimental

Reactions were carried out in a 32 × 197 mm. cylindrical quartz cell, 158-ml. volume, contained in an air thermostat. The whole cell was uniformly illuminated. Pressure changes were measured by a quartz spiral gage. At the end of a run, the contents of the reaction vessel were separated by use of a Toepler pump into a volatile fraction, non-condensable at −120°, and a non-volatile sample, the remainder. Analyses of both fractions were made by a consolidated mass spectrometer.

Di-*t*-butyl peroxide was obtained from Shell Chemical Co. and was further purified by bulb-to-bulb distillation under vacuum. The refractive index was found to be n^2D 1.3888. This compares well with published values of 1.3889[4] and 1.3890.[5] Butadiene was Matheson C.P. grade.

A Hanovia Type A burner operated on direct current was used in all the experiments as the light source. A potassium triiodide solution was used as a filter to limit the radiation to the 2537 Å. region in some of the runs.

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[1] Based on a portion of a thesis presented by W. M. Graven in partial satisfaction of the requirements for the degree of Doctor of Philosophy in the University of California.

[2] M. Barak and D. Style, *Nature*, **135**, 307 (1935).

[3] E. R. Bell, F. F. Rust and W. E. Vaughan, THIS JOURNAL, **72**, 337 (1950).

[4] L. M. Dorfman and Z. W. Salsburg, *ibid.*, **73**, 255 (1951).

[5] J. H. Raley, F. F. Rust and W. E. Vaughan, *ibid.*, **70**, 88 (1948).

Results and Discussion

Absorption Spectrum of Di-*t*-butyl Peroxide.—The absorption spectrum of di-*t*-butyl peroxide in isoöctane solution measured by a Beckman spectrophotometer shows regularly increasing absorption in the measured region, 3400 to 2200 Å., without any evidence of structure.[3] However, in order to establish the primary process in the gaseous state, it was felt that the gaseous absorption spectrum determined with an instrument of greater resolution would be of value. Also, quantitative data on gaseous absorption were needed for the application of actinometry in the determination of quantum yields. The spectrum was determined in the region 2200–3200 Å. using a Bausch and Lomb Large Littrow Spectrograph. The pressure of peroxide was 27 mm. and a 56-cm. light path was used. Quantitative measurements were obtained by using calibrated screens as previously described.[6] Measurements of spectral plate densities were made with an Applied Research Laboratory projection comparator-densitometer. The absorption coefficients obtained are shown in Table I.

TABLE I

ULTRAVIOLET ABSORPTION SPECTRUM OF GASEOUS DI-*t*-BUTYL PEROXIDE

Wave length, Å.	2447	2535	2625	2699	2753
Absorption coeff. (l. mole^{-1} cm.$^{-1}$)	7.1	6.4	5.4	4.5	4.0
Wave length, Å.	2800	2894	3011	3051	
Absorption coeff. (l. mole^{-1} cm.$^{-1}$)	3.3	2.5	1.6	0.9	

No evidence for any structure in the spectrum was obtained. Although it is possible that the spectrum is not a true continuum, and the use of lower pressures and an instrument of greater resolving power might reveal some structure, this is hardly to be expected. In this connection it may be observed that the spectrum of hydrogen peroxide is without structure and it is almost certainly a true continuum.[7,8] Since light absorption takes place in the O–O bond, and since the energy available per quantum in the light absorption region is far in excess of the bond dissociation energy, less than 40 kcal. per mole,[5,9] the most reasonable expectation is that absorption of light leads to a rupture of the O–O bond with a primary photochemical efficiency of unity.

$$(CH_3)_3COOC(CH_3)_3 + h\nu \longrightarrow 2(CH_3)_3CO \qquad (1)$$

This reaction is analogous to the primary process which has been well established for gaseous H_2O_2 photolysis.[10]

Photodecomposition of Di-*t*-butyl Peroxide.—The peroxide was photolyzed at temperatures ranging from 30 to 120°, Table II. The dark reaction was at all temperatures negligible compared to the photochemical reaction. Acetone, ethane, carbon monoxide, methane, biacetyl and *t*-butyl alcohol were the only products formed in quantities large enough for identification by mass spectrometry. Presumably carbon monoxide, biacetyl and some of the ethane are formed from the decomposition of acetone subsequent to its formation by the decomposition of *t*-butoxy radical[5]

$$(CH_3)_3CO \longrightarrow (CH_3)_2CO + CH_3 \qquad (2)$$

In the experiments of Dorfman and Salsburg where acetone was frequently removed from the radiation zone, no carbon monoxide was found in the products.[4]

TABLE II

PRODUCTS IN DI-*t*-BUTYL PEROXIDE AND ACETONE PHOTOLYSES

					Quantities in moles × 10^4					
T, °C.	Time, min.	Reactant	Initial quantity	Decomposed quantity	CO	MeH	*t*-BuOH	Me_2CO	EtH	Me_2CO/EtH
					Full arc					
33	40	D-*t*-bP	2.86[a]	0.95	0.13	0.026	0.054	1.48[b]	0.72[b]	2.1
34	30	D-*t*-bP	2.88	0.82	.06	.017		1.14	.51	2.2
65	40	D-*t*-bP	2.63	1.05	.19	.029	.033	1.53	.72	2.1
75	40	D-*t*-bP	2.53	.95	.22	.030	.052	1.53	.73	2.1
100	30	D-*t*-bP	2.64	.81	.18	.022	.018	1.10	.56	2.0
120	30	D-*t*-bP	2.10	.87	.23	.025	Trace	1.00	.49	2.0
					2537 Å. region					
80	60	Acetone	2.34	0.25	0.19	0.006			0.26	
40	60	D-*t*-bP	2.48		.00	.002	0	0.54	.26	2.1
60	60	D-*t*-bP	2.47	.30	.01	.002	Trace	.55	.26	2.1
80	60	D-*t*-bP	2.30	.26	.02	.002	0	.55	.25	2.2
100	60	Acetone	2.20		.20	.006			.23	
100	60	D-*t*-bP	2.09		.02	.003	0	.39	.21	1.9
100	60	Acetone	2.38	.32	.34	.011			.34	
100	60	D-*t*-bP	2.33	.33	.06	.004	0	.64	.33	1.9
100	60	Acetone	2.13		.38	.011			.41	
100	60	D-*t*-bP	2.18	.48	.10	.006	0	.81	.43	1.9

[a] This corresponds to a pressure of 27.3 mm. [b] Values relating to peroxide in this column are corrected for photodecomposition of acetone.

At temperatures above about 70° the decomposi-

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(6) R. K. Brinton and D. H. Volman, *J. Chem. Phys.*, **19**, 1394 (1951).

(7) H. C. Urey, L. H. Dawsey and F. O. Rice, THIS JOURNAL, **61**, 1371 (1939).

(8) R. B. Holt, C. K. McLane and O. Oldenberg, *J. Chem. Phys.*, **16**, 225 (1948).

(9) R. K. Brinton and D. H. Volman, *ibid.*, **20**, 25 (1952).

(10) D. H. Volman, *ibid.*, **17**, 947 (1949).

tion of acetone[11] may be expressed by the over-all equation

$$(CH_3)_2CO + h\nu \longrightarrow C_2H_6 + CO \qquad (3)$$

with a quantum efficiency of unity over a wide range of intensity and concentration. The decomposition products may be corrected for the contribution from acetone decomposition by subtracting from the total ethane found an amount equivalent to the carbon monoxide found and adding this amount to the total acetone found. These "corrected" amounts of acetone and ethane and the ratio between them are listed in the last three columns of Table II. The approximate two to one ratio found is in accord with the proposed thermal[5] and photochemical[4] mechanisms. The source of ethane is then

$$CH_3 + CH_3 \longrightarrow C_2H_6 \qquad (4)$$

Methane and *t*-butyl alcohol may be accounted for by the usual hydrogen atom abstraction mechanisms. A complete account of the contribution of decomposing acetone should take into consideration the abstraction of H atom by methyl and the formation of biacetyl from acetyl radicals. However, on account of the relatively small quantities of these products, such a consideration could not affect the values of the ratios found significantly. It may be observed that reaction of methyl and acetyl to form acetone cannot affect the ratio.

Quantum yields may be calculated from the data of Table II using acetone as the actinometer. The intensity of absorbed light was calculated on assumption of a quantum yield of unity for ethane production during acetone photodecomposition. From Table II it may be seen that where data are available for comparison, the ethane yield corresponds to the experimentally determined quantity of acetone decomposition more closely than does the carbon monoxide yield. The acetone experiments were carried out just prior to the peroxide experiment following so that the incident intensity could be considered constant. Lambert and Beers law was used in the calculation with the absorption coefficient of acetone taken as 7.0[12] and the absorption coefficient of di-*t*-butyl peroxide taken as 6.4 from our determination at 2537 Å. This approximate equivalence in the absorption coefficients and concentrations of absorbing compound makes corrections for reflections unnecessary considering the limitations of the experiments. The results obtained are shown in Table III.

TABLE III

QUANTUM YIELDS IN DI-*t*-BUTYL PEROXIDE PHOTODECOMPOSITION AT 2537 Å.

Temp., °C.	I_{abs}, Einsteins, min.$^{-1}$ × 10^7	t-Bu_2O_2 decomposition	Me_2CO formation	EtH formation	MeH formation
40	4.3		2.1	1.0	0.006
60	4.3	1.2	2.1	1.0	.007
80	4.1	1.1	2.2	1.0	.009
100	3.5		1.9	1.0	.012
100	5.4	1.0	2.0	1.0	.014
100	6.6	1.2	2.1	1.1	.015

The quantum yield values substantiate the essential features of the mechanism given. No appreciable effects attributable to intensity can be observed in the experiments at 100° where the intensity was varied. However, these intensities are already quite high and the variation is only over a twofold range. Dorfman and Salsburg[4] have reported an appreciable dependence of methane formation as a function of intensity. Their results are reasonable and to be expected since their intensities were far lower.

Polymerization of Butadiene.—Since acetone is formed in the photodecomposition of the peroxide and its subsequent photodecomposition is inherent under the experimental methods used, the polymerization has been studied with both peroxide and acetone as initiators. In all experiments, the formation of ethane and methane is negligible. Therefore the only probable reactions of radicals derived from di-*t*-butyl peroxide and acetone in these experiments is the decomposition of *t*-butoxy and acetyl or the addition of these radicals and methyl to butadiene. Butadiene does not show appreciable absorption above about 2200 Å. and so polymerization by light absorption by butadiene is not very probable in this work. We have confirmed this point by finding only negligible polymerization for a system of butadiene vapor irradiated for very long periods.

Figure 1 shows the effect of butadiene concentration on the polymerization rate of butadiene–acetone and butadiene–peroxide mixtures at 60°.

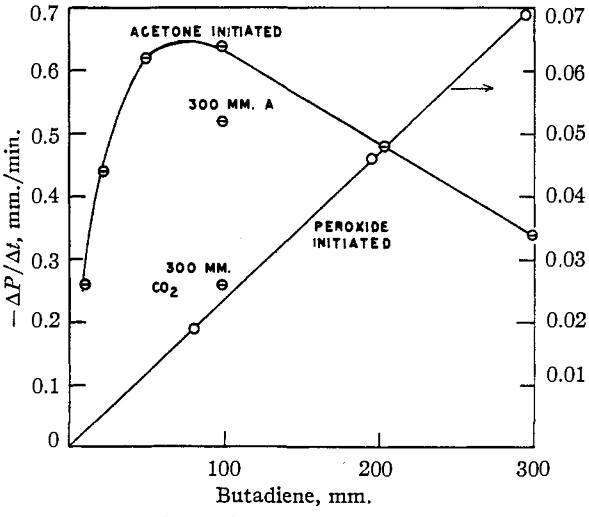

Fig. 1.—Effect of butadiene pressure on polymerization rate: acetone, 46.0 mm.; di-*t*-butyl peroxide, 23.5 mm.

The peroxide results were obtained with radiation limited to the 2537 Å. region while the full arc radiation was used in the acetone experiments. The peroxide results are consistent with an interpretation of a quantum efficiency of unity for the primary dissociation into free radicals. The results with acetone suggest that deactivation of a photoactivated state is involved. The primary step must be at least in part

$$(CH_3)_2CO + h\nu \longrightarrow (CH_3)_2CO^* \qquad (5)$$

This is followed by

$$(CH_3)_2CO^* \longrightarrow CH_3CO + CH_3 \qquad (6)$$

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[11] D. S. Herr and W. A. Noyes, Jr., THIS JOURNAL, **62**, 2052 (1940).

[12] C. W. Porter and C. Iddings, *ibid.*, **48**, 40 (1926).

or

$$(CH_3)_2CO^* + X \longrightarrow (CH_3)_2CO + X^* \tag{7}$$

where X is any third body. It might be argued that the effect observed in curve I can be explained by the reaction of CH_3CO with butadiene becoming more prominent at higher butadiene pressures in view of the competitive process

$$CH_3CO \longrightarrow CH_3 + CO \tag{8}$$

However, the decrease in polymerization rate observed on adding foreign gases argon and CO_2 does not support this point of view but is consistent with the interpretation of a photoactivated state. Similar points of view have been proposed to explain results on the photolysis of acetone in the presence of iodine.[13,14] Very recently Martin and Sutton[15] have shown that carbon dioxide does not influence the quantum yield of acetone decomposition in an acetone–carbon dioxide system. Likewise acetone itself does not seem to influence the quantum yield of photodecomposition. These authors postulate that, in the presence of iodine, photoactivated acetone is transferred to a second excited state which in turn may be deactivated in the usual manner by any third body. The specific mechanism of this secondary activation may involve a complex $(CH_3)_2CO{\cdot}I_2$. It may be pointed out that butadiene may act by an analogous mechanism. That is, complex formation between butadiene and acetone of the kind inherent in an incipient Diels–Alder reaction may play a role.[16]

The polymerization rate was studied as a function of temperature at constant absorbed light intensity. The results are shown in Fig. 2. The over-all activation energies calculated are 5.8 ± 1.0 kcal./mole for the di-*t*-butyl peroxide initiated polymerization and 5.0 ± 1.0 kcal./mole for the acetone initiated reaction. These values are in agreement with the estimate of 5.5 kcal./mole for the activation energy of propagation in the gas phase photopolymerization of butadiene.[17] 2.8 kcal./mole has been reported for the activation energy of propagation in butadiene polymerization induced by the thermal decomposition of di-*t*-butyl peroxide.[18] However, this result depended on the activation energy for di-*t*-butyl peroxide decomposition. Our later determination of this value[9] leads to an activation energy for chain propagation of about 4 kcal./mole.

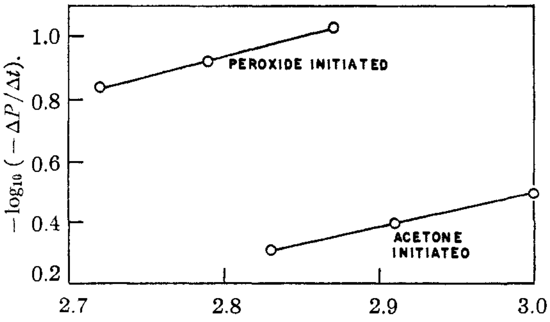

Fig. 2.—Effect of temperature on initial polymerization rate: acetone 2.26; butadiene 9.75; di-*t*-butyl peroxide 1.15; butadiene 10.4 moles liter^{-1} × 10^3.

At constant rate of initiation of polymerization, constant light intensity, the empirical equation for the induced photochemical polymerization may be written

$$-(\mathrm{d}P/\mathrm{d}t) = k_9[\mathrm{M}] \tag{9}$$

where $\mathrm{d}P/\mathrm{d}t$ refers to the rate of polymerization and [M] to the concentration of monomer, butadiene. For E_9 we take the average of the acetone and peroxide induced values, 5.4 ± 1.4 kcal./mole. k_9 will in general depend upon an initiation rate constant, a termination rate constant and a propagation rate constant, k_p. For photochemical initiation the initiation rate constant is a function of intensity only and therefore has zero activation energy. Termination activation energies in polymerization are generally nearly zero. Since k_9 generally will be first power in k_p,[19] E_9 may be considered as substantially equal to E_p, the activation energy for chain propagation.

Decomposition of *t*-Butoxy Radical.—Equation (2) combined with the equation representing the attachment of a *t*-butoxy radical to butadiene in the polymerization step

$$(CH_3)_3CO + M \longrightarrow (CH_3)_3COM \tag{10}$$

leads to the equation

$$\frac{\mathrm{d}[(CH_3)_2CO]/\mathrm{d}t}{\mathrm{d}[(CH_3)_3COM]/\mathrm{d}t} = \frac{R_\mathrm{A}}{R_\mathrm{B}} = \frac{k_2}{k_{10}[\mathrm{M}]} \tag{11}$$

R_A may be determined by mass spectrometer analysis for acetone formed in the presence of butadiene. In the absence of butadiene all of the *t*-butoxy radical decomposes by eq. (2). In the presence of butadiene, *t*-butoxy radical can either decompose or attach to a butadiene molecule. The rate of attachment of *t*-butoxy to butadiene is then given by the difference in the amounts of acetone formed in the absence and in the presence of butadiene. Thus R_B can be determined. A plot of $R_\mathrm{B}/R_\mathrm{A}$ against butadiene concentration should then yield a straight line. The results obtained at various temperatures are shown in Fig. 3. An Arrhenius plot of the data of Fig. 3 leads to $E_2 - E_{10} = 5.8$ kcal./mole. If the value of $E_{10} =$ 5.4 kcal. is used, then $E_2 = 11.2 \pm 2$ kcal./mole.

Decomposition of Acetyl Radical.—Likewise for the acetone initiated polymerization we may write

$$CH_3CO + M \longrightarrow CH_3COM \tag{12}$$

Combined with equation (8) this gives

$$\frac{\mathrm{d}[CH_3COM]/\mathrm{d}t}{\mathrm{d}[CO]/\mathrm{d}t} = \frac{R_\mathrm{C}}{R_\mathrm{D}} = \frac{k_{12}[\mathrm{M}]}{k_8} \tag{13}$$

As before R_D is determined by mass spectrometric analysis of the carbon monoxide formed in the presence of butadiene. R_C is determined by the differences in carbon monoxide formation in the absence and in the presence of butadiene. These runs were carried to completion since the influence

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[13] W. A. Noyes, Jr., *J. Phys. Colloid Chem.*, **55**, 925 (1951).

[14] J. N. Pitts, Jr., and F. E. Blacet, THIS JOURNAL, **74**, 455 (1952).

[15] C. R. Martin and G. C. Sutton, *Trans. Faraday Soc.*, **48**, 812 (1952).

[16] R. B. Woodward, THIS JOURNAL, **64**, 3058 (1942).

[17] G. Gee, *Trans. Faraday Soc.*, **34**, 712 (1938).

[18] D. H. Volman, *J. Chem. Phys.*, **19**, 668 (1951).

[19] See for example, K. J. Laidler, "Chemical Kinetics," McGraw-Hill Book Co., New York, N. Y., 1950, p. 345.

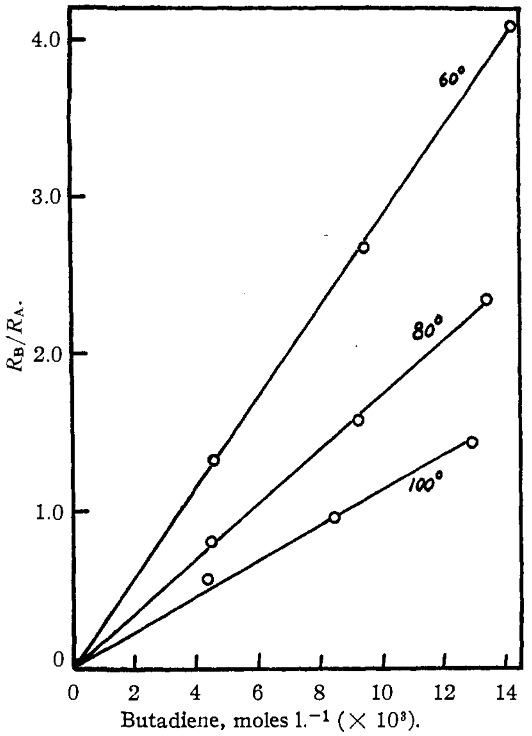

Fig. 3.—Effect of butadiene concentration on acetone formation in peroxide–butadiene mixtures: 2537 Å. region, di-*t*-butyl peroxide, 1.15 × 10^{-3} moles l.$^{-1}$.

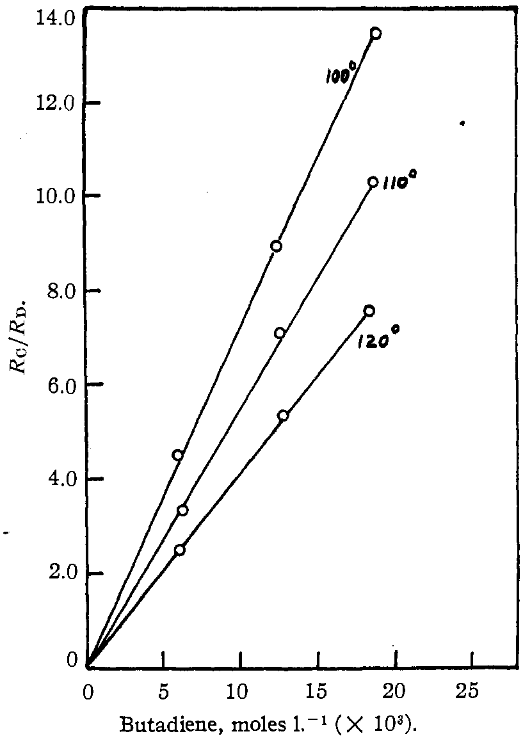

Fig. 4.—Effect of butadiene concentration on carbon monoxide formation in acetone–butadiene mixtures: unfiltered light; acetone, 1.15 × 10^{-3} moles l.$^{-1}$.

of pressure on the yield of acetyl radicals, eq. (6) and (7), would not allow R_C to be calculated from runs of short duration. The extent of reaction is not important for either equation (13) or (11) providing [M] does not change significantly and, hence, amounts of product may be substituted for the rates. Plots of R_C/R_D *vs.* [M] for various temperatures are shown in Fig. 4, and the straight lines obtained are a confirmation of the treatment. An Arrhenius plot of the slopes of Fig. 4 leads to $E_8 - E_{12} = 8.1$ kcal./mole. Taking E_{12} as again equal to 5.4, $E_8 = 13.5 \pm 2.0$ kcal./mole. This result is in substantial agreement with the value of 16 ± 2 kcal./mole reported by Marcotte and Noyes.[20]

Primary Process in Acetone Photolysis.—Strong arguments in support of a completely free radical mechanism for acetone photolysis have been presented by various workers[14,21-23] Arguments in favor of some intramolecular reaction forming CO and ethane have also been advanced.[24,25] The photodecomposition of acetone in the presence of butadiene is in accord with a completely free radical mechanism. In Table IV the yields of carbon monoxide and ethane are shown at various temperatures for acetone–butadiene mixtures. The striking feature of these results is the elimination of C_2H_6 as a product as the pressure of butadiene increases. Thus not only is C_2H_6 not formed intramolecularly but the combination of methyl radicals to form ethane is virtually eliminated. It may be presumed that at the higher butadiene pressures all of the methyl radicals formed are trapped by butadiene. Likewise, the yield of CO is greatly reduced. This may be readily explained by a similar action of butadiene on acetyl radicals competing with the decomposition of acetyl radicals and the deactivation of photoactivated acetone by butadiene. Both of these effects would reduce CO yield. However, it is clearly evident that under conditions where all the methyl radicals are trapped, CO may still be formed. If any of this CO were formed by an intramolecular process, an equivalent amount of ethane would be expected.

TABLE IV

IRRADIATION OF ACETONE–BUTADIENE MIXTURES

Acetone pressure = 26 mm.

		Product (moles × 10^4)		
T, °C.	Butadiene P(mm.)	CO	C_2H_6	CH_4
100	0	2.09	2.00	0.06[a]
100	139	0.39	0.04	.04
100	289	.22	.01	.02
100	438	.15	.00	.01
110	149	.50	.05	.07
110	302	.26	.01	.02
110	445	.19	.00	.01
120	0	2.18	1.97	.07[a]
120	147	.61	.06	.11
120	313	.34	.01	.02
120	451	.25	.00	.01

[a] 95% decomposition of acetone.

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[20] F. B. Marcotte and W. A. Noyes, Jr., THIS JOURNAL, **74**, 783 (1952).

[21] L. M. Dorfman and W. A. Noyes, Jr., *J. Chem. Phys.*, **16**, 557 (1948).

[22] W. A. Noyes, Jr., and L. M. Dorfman, *ibid.*, **16**, 788 (1948).

[23] S. W. Benson and C. W. Falterman, *ibid.*, **20**, 201 (1952).

[24] R. Spence and W. Wild, *J. Chem. Soc.*, 352 (1937).

[25] D. H. Volman, P. A. Leighton, F. E. Blacet and R. K. Brinton, *J. Chem. Phys.*, **18**, 203 (1950).

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DAVIS, CALIFORNIA

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF ILLINOIS INSTITUTE OF TECHNOLOGY]

Kinetics of the Raney Nickel Catalyzed Hydrogenation of Crotonic Acid

BY FRED L. MORRITZ,[1] EUGENE LIEBER AND RICHARD B. BERNSTEIN

RECEIVED DECEMBER 22, 1952

The kinetics of the Raney nickel-catalyzed hydrogenation of crotonic acid in ethanol solution have been studied using an isobaric hydrogenation apparatus. It was found that the rate could be expressed accurately by a Langmuir-type equation of the form: $-\,dc/dt = \{kaAPc/[V(1 + bc)]\}\{1/[1 + r(c_0 - c)]\}$, where V is the volume of solvent; c is the concentration of acceptor; A is the surface area of catalyst; P is the hydrogen pressure; k is the specific rate constant; a and b are adsorption coefficients for acceptor; and r is the coefficient for retardation by product. The kinetics appear zero order with respect to crotonic acid for the initial portion of the hydrogenation and first order during the final stages. The reaction is retarded by the product, butyric acid. The kinetic data may be interpreted satisfactorily by a Balandin type dual-site mechanism.

Introduction

The catalytic hydrogenation of a carbon–carbon double bond has often been assumed to follow zero-order kinetics with respect to the hydrogen acceptor.[2–6] However there are several examples of hydrogenations which appear to follow intermediate or first-order rate laws.[7–11] In the case of the hydrogenation of crotonic acid, Lebedev, *et al.*,[12] and Maxted[13] reported zero order, while Fokin[14] found first-order behavior. Balandin,[15] in attempting to reconcile these differences, postulated a rate law based on non-competitive adsorption of the reactants on two types of active centers. The present study was undertaken to obtain precise kinetic data on the hydrogenation of crotonic acid over Raney nickel catalyst in order to examine the validity of the several plausible adsorption mechanisms for catalytic hydrogenation.

Experimental

Raney Nickel Catalyst—Modified Form.—The leaching and digestion procedures of Adkins and Billica[16] were followed using 125 g. of Raney alloy. The alkaline solution was decanted and the catalyst washed 30 times with 1-l. portions of water.

A 2-l. portion of water was added to the catalyst which was held at 100° for 3–4 hr. with vigorous stirring during the last 1/2 hr. to remove excess hydrogen. After decantation, the catalyst was washed 6 times with 500-ml. portions of ethanol, and stored under absolute ethanol in a glass stoppered bottle.

The basis for measurement of the amount of catalyst was its volume after a 5-min. centrifugation.[17]

Although the procedure was followed rigorously, it was impossible to duplicate precisely the activities of the catalysts in separate preparations. It was thus necessary that each of a series of related experiments be made using the same batch of catalyst. Due to the instability of the catalyst, series were completed in 1–2 days, during which time the reproducibility of the kinetic data was satisfactory.

The surface area of a typical catalyst was determined by the adsorption method[18] using myristic acid; the surface area of a typical batch was 30 $m.^2/g$. Using a similar technique it was found that crotonic acid was adsorbed in multilayers. The adsorption isotherm was of the Freundlich type.

Materials.—Tank hydrogen was passed through a "Deoxo" purifier. Absolute ethanol was used: $n^{25}D$ 1.3592. *trans*-Crotonic acid (Tennessee-Eastman Co.) was purified by two crystallizations from light-boiling petroleum ether. The crotonic acid was obtained as white needles, m.p. 72–72.5° (uncor.); lit. 72°. By electrometric titration, the neutralization equivalent was 86.7; theoretical 86.1. Fractional distillation of the product mixture yielded butyric acid: b.p. 163°, $n^{20}D$ 1.3987. Neutralization of the cold, filtered product mixture with NaOH indicated a butyric acid yield of 97.5% based on weight of sodium butyrate recovered. No evidence for esterification was found.

The Isobaric Hydrogenation Apparatus. (**Fig.** 1).—A 4-l. tank (A), from a Parr hydrogenation apparatus, used as a hydrogen reservoir, was connected to an open-end Hg manometer (B) (Merriam Co.) and to a solenoid valve (C) (General Controls Co.). The solenoid valve was waxed into a Pyrex manifold, which included a silica-gel trap (S), a 500-ml. ballast bulb (D), a mercury manostat (E), a manometer (F), and the reaction bottle (G) (a 250-ml. suction flask). The reaction flask was connected to the apparatus by Tygon tubing. Contacts (H) from the manostat led to the input of a thyratron circuit connected to the solenoid (J). The shaking carriage, in which the reaction flask was mounted, was taken from a Parr apparatus, and could be operated at 260 or 380 cycles/min. The greater part of the flask was immersed in a thermostat.

The flask was fitted with a "breaking tube" (see insert). A Pyrex tube (K), with a thin bottom, was attached to the neoprene stopper (L). Through the brass sleeve (M) a movable brass rod (N) with a neoprene gasket (O) was held against the lower end of the brass sleeve by spring (P). Pressure exerted at the top of the brass rod forces it downward, breaking tube (K). When the pressure on rod (N) is released, the spring forces it up and the gasket is again seated against the bottom of sleeve (M). An inert fluorocarbon grease, BFE-3 (Carbide and Carbon Chem. Corp.)

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[1] Taken from a Ph.D. thesis submitted to the Graduate School of Illinois Institute of Technology.

[2] M. G. Vavon, *Compt. rend.*, **152**, 1675 (1911).

[3] R. Willstätter, *Ber.*, **45**, 1471 (1912).

[4] S. V. Lebedev, *J. Russ. Phys. Chem. Soc.*, **48**, 1002 (1916).

[5] J. S. Salkind, *ibid.*, **52**, 191 (1920); *C. A.*, **17**, 1453 (1923).

[6] E. F. Armstrong and T. P. Hilditch, *Proc. Roy. Soc.* (*London*), **A98**, 27 (1920).

[7] A. A. Zinovyev, *Zhur. Priklad. Khim.*, **23**, 99 (1950); *C. A.*, **44**, 4320 (1950).

[8] S. Ueno and S. Tsuda, *J. Soc. Chem. Ind. Japan*, **46**, 481 (1943).

[9] A. Kailan and F. Hartel, *Monatsh.*, **70**, 329 (1937).

[10] A. Kailan and O. Albert, *ibid.*, **72**, 169 (1938).

[11] F. A. Vandenheuvel, *Anal. Chem.*, **24**, 847 (1952).

[12] S. V. Lebedev, G. G. Kobliansky and A. A. Yabulchik, *J. Chem. Soc.*, 417 (1925).

[13] E. B. Maxted, "Advances in Catalysis," Vol. III, Interscience Publ., Inc., New York, N. Y., 1951.

[14] S. Fokin, *J. Russ. Phys. Chem. Soc.*, **40**, 276, 309 (1908); *C. A.*, **2**, 2896 (1908).

[15] A. A. Balandin, *Bull. acad. sci. U.R.S.S., Classe sci. chem.*, 339 (1945).

[16] H. Adkins and H. R. Billica, THIS JOURNAL, **70**, 695 (1948).

[17] D. R. Levering, F. L. Morritz and E. Lieber, *ibid.*, **72**, 1190 (1950).

[18] H. A. Smith and J. F. Fuzek, *ibid.*, **68**, 229 (1946).