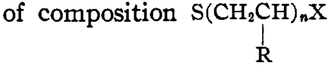
have remained sensibly constant. Hence, experimental difficulties make it practical to use Equation (1) only for solvents having transfer constants of about 5 or less.

Table II shows that alkoxyl group substitution does not change the activity of primary mercaptans and, together with other work, that transfer constants of primary mercaptans are independent of their molecular weight.[11] Thus, *n*-amyl mercaptan has a transfer constant of 20,[6] and *n*-butyl mercaptan of 22 ± 3.[12] The tertiary mercaptan is much less reactive than the primary mercaptans while ethyl thioglycolate is by far the most reactive mercaptan known.

Previous work[2,3,5] has shown that transfer constants of relatively unreactive solvents increase with increasing temperature. For the mercaptans, the transfer constants decrease with increasing temperature and the activation energy for chain transfer is lower than for chain growth.

Transfer theory demands the production of a series of compounds of composition  $\mathrm{S(CH_2\underset{\underset{R}{|}}{C}H)_nX}$ from an unsaturate $\mathrm{RCH{=}CH_2}$ and a solvent SX, where X is removed by radical transfer, and *n* is 1 or greater. The proportions of the products will depend on the nature and concentrations of reactants but in general the mole fraction of *n*-mer must decrease as *n* increases. Mercaptan addition products with $n = 1$ have long been known. The present work showed that the reaction of equal moles of styrene and dodecyl mercaptan gave a product with $n = 1$ and a smaller amount of mixed products averaging $n = 2.7$. With this system, separation of the products by distillation could not be made sufficiently precise to enable calculation of the transfer constants of the individual radicals. A later paper will describe the separation of the reaction products of low molecular weight mercaptans with styrene and the calculation of the transfer constants of the individual radicals. These phenomena have been described previously in detail for carbon tetrachloride[3,4] in which case the pure 1:1 compound has not been isolated.

Summary

The abilities of four mercaptans to supply a hydrogen atom to the substituted benzyl radical in polymerization have been compared by two methods, by their effect in reducing the molecular weight of the polymer and by the relative rates of reaction of monomer and mercaptan. Results by the two methods are in agreement. Mercaptans possess a high activity toward radicals, the substituted benzyl radical preferring transfer with the mercaptan to reaction with styrene. α-Methyl group substitution decreases and α-carboethoxy substitution increases the reactivity of a mercaptan toward radicals.

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[11] In emulsion polymerization, the decreased water solubility of higher molecular weight mercaptans decreases their effective regulating ability. The converse may be true for alkoxy substituted mercaptans; *cf.* W. V. Smith, THIS JOURNAL, **68**, 2064 (1946).

[12] Walling, *ibid.*, **70**, 2561 (1948).

[CONTRIBUTION NO. 48 FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF TENNESSEE]

Kinetics of Heterogeneous Reactions with Special Reference to Catalytic Hydrogenation

BY JOHN F. FUZEK AND HILTON A. SMITH

A great many articles have been published dealing with the kinetics of certain catalytic reactions.[1] Most of the measurements have involved the reaction of gaseous materials on catalytic surfaces, reaction rate constants having been calculated from the pressure drops in the systems used.

A critical examination of the kinetics of such reactions leads to the conclusion that the rate constants calculated in this manner depend on the volume of the gaseous system used. In spite of this, comparison of such experimental constants with equations which do not involve the volume of the system are made. A true constant is obtained only when the rate equation is in the form

$$\frac{\mathrm{d}p_x}{\mathrm{d}t} = \frac{k}{V}\,p_x{}^a$$

rather than the usual

$$\frac{\mathrm{d}p_x}{\mathrm{d}t} = k'p_x{}^a$$

where p is the pressure of the gas x, and a is the reaction order.

It is of some interest to compare experimental results of catalytic reactions using gaseous systems of different volumes. On examining the literature, it was noted that sometimes the volume of the system studied for a given reaction was not even specified, and reliable data taken for different volumes were not found. Therefore, for sake of such comparison, several catalytic hydrogenation reactions were run both at high and low pressures using nickel and platinum catalysts.

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[1] Hinshelwood, "The Kinetics of Chemical Change," Oxford University Press, Oxford, England, 1940, Chapter VIII; Pease, "Equilibrium and Kinetics of Gas Reactions," Princeton University Press, Princeton, New Jersey, 1942, Chapter IX; Glasstone, Laidler, and Eyring, "The Theory of Rate Processes," McGraw-Hill Book Co., Inc., New York, N. Y., 1941, Chapter VII.

Experimental

Raney nickel and Adams platinum catalysts were prepared according to the directions given in "Organic Syntheses."[2,3]

The pure solvents, **glacial acetic acid** and **ethanol**, were prepared from C. P. reagent glacial acetic acid and absolute ethanol by fractionation in a five-foot helix-packed column.

Benzene was purified by fractionation of thiophene-free Merck reagent benzene in a five-foot helix-packed column.

Benzoic acid and **palmitic acid** were Eastman Kodak Company white label grade. They were used without further purification.

Pure **dipentene** was furnished by the Hercules Powder Company of Wilmington, Delaware. The material was reported to have the following constants: boiling point 110.5° at 100 mm.; $n^{20}\text{D}$ 1.4730; $\alpha^{20}\gamma$ 0.8448.

***d*-Limonene** was purified by distillation of Eastman Kodak Company technical product in an eight-foot Vigreux column. The portion used boiled at 176.7° at 740 mm. pressure, constants: $n^{20}\text{D}$ 1.4729, $\alpha^{20}\text{D}$ 104° 40′.

The procedure for making low-pressure hydrogenations using platinum catalyst was the same as that previously employed.[4] With nickel catalyst, a similar procedure was followed, except that an estimated 0.5 g. of nickel catalyst was removed from the bottle in which it was stored under ethanol, and added to the reaction bottle before hydrogenation. After the reduction was complete, the hydrogenated product and solvent were filtered from the catalyst, and the latter dried and weighed under an atmosphere of carbon dioxide.

The details of the procedure for high pressure runs will be given in a subsequent paper. The method of determining the weight of catalyst used was the same as that for the low-pressure reductions.

The volume of the tank supplied with the Parr Catalytic Reduction Apparatus was 4.020 liters. Two additional tanks were constructed having volumes of 1.510 and 0.875 liters. These could be fitted into the apparatus in place of the standard tank, or any combination of tanks could be used. The volume of the empty reaction bottle and connections was 0.460 liter. The volume of each tank was determined by weighing the water required to fill it. The volume of the empty reaction bottle plus connections was found by admitting a known volume of gas at a measured pressure to the system filled with gas at a known pressure, and calculating the volume from the pressure change using Boyle's law. The volumes of the four high-pressure bombs used were 45, 145, 245, and 630 ml. The volume of the gage and connections was 11 ml.

All hydrogenations were carried out at room temperature (26–28°).

Experimental Calculations and Results

It has been demonstrated in the conventional manner that the hydrogenation of benzene and benzoic acid over platinum catalyst in glacial acetic acid solvent is first order with respect to hydrogen pressure, zero order with respect to the concentration of hydrogen acceptor, and directly proportional to the amount of catalyst used.[4] The same dependence is found for the low-pressure hydrogenations of dipentene or *d*-limonene on Adams platinum catalyst in glacial acetic acid, and for the low- or high-pressure (1000 pounds per square inch) hydrogenation of dipentene or *d*-limonene on Raney nickel when ethanol is used as solvent. A similar situation exists when dipentene or *d*-limonene are hydrogenated at high pressures without solvent but in the presence of a small amount (0.0004 mole per gram of catalyst) of palmitic acid. The rate of the reaction is therefore given by the expression

$$-\frac{dp_{H_2}}{dt} = \frac{k}{V}p_{H_2}$$

which, when integrated gives

$$\log\frac{p^0_{H_2}}{p_{H_2}} = \frac{kt}{2.303V}$$

To get the values of k, the slopes of the straight lines obtained by plotting $\log p^0_{H_2}/p_{H_2}$ against t were multiplied by $2.303V$. These constants, all referred to one gram of catalyst, are given in Table I, together with the material being hydrogenated, the conditions of the reaction, and the volume of the hydrogen gas in the system during the reduc-

TABLE I

FIRST ORDER RATE CONSTANTS FOR SEVERAL CATALYTIC HYDROGENATION REACTIONS

Reaction conditions	Hydrogen volume, liters	k,[a] liter min.$^{-1}$	k', min.$^{-1}$
Hydrogenation of 0.05 mole of benzene on 0.45–0.50 g. of PtO_2; initial pressure = 64 p. s. i.; solvent, 50 ml. of glacial acetic acid	1.29	0.199	0.154
	1.92	.213	.111
	2.80	.206	.0736
	4.43	.210	.0475
	4.43	.215	.0486
	5.95	.194	.0326
Hydrogenation of 0.05 mole of benzoic acid on 0.2 g. of PtO_2; initial pressure, 64 p. s. i.; solvent, 50 ml. of glacial acetic acid	1.29	0.0942	0.0730
	1.29	.0922	.0715
	1.92	.0928	.0483
	2.80	.0924	.0330
	4.43	.0908	.0205
	5.95	.0904	.0152
Hydrogenation of 0.05 mole of dipentene on 0.01 g. of PtO_2; initial pressure, 64 p. s. i.; solvent. 50 ml. of glacial acetic acid	1.29	3.78	2.930
	1.92	3.57	1.860
	2.80	3.47	1.240
	4.43	3.78	0.853
	5.95	3.57	0.600
Hydrogenation of 0.05 mole of dipentene on 0.540–0.676 g. of Raney nickel; initial pressure, 64 p. s. i.; solvent, 10 ml. of absolute ethanol	1.32	0.00319	0.0242
	1.95	.00339	.0174
	2.83	.00362	.0128
	4.46	.00321	.0072
	5.98	.00323	.0054
Hydrogenation of 0.05 mole of *d*-limonene on 0.366–0.611 g. of Raney nickel; initial pressure, 1000 p. s. i.; solvent, 10 ml. of absolute ethanol	0.036	0.00619	0.1720
	.146	.00662	.0454
	.236	.00703	.0298
	.631	.00606	.0096
Hydrogenation of 0.05 mole of *d*-limonene on 0.377–0.487 g. of Raney nickel plus 0.0002 mole of palmitic acid; no solvent; initial pressure = 1000 p. s. i.	0.046	0.00212	0.0460
	.156	.00187	.0120
	.246	.00197	.0080
	.641	.00179	.0028

[a] All rate constants are referred to 1 g. of platinum dioxide or 1 g. of Raney nickel catalysts by multiplying the rate constant actually obtained by the reciprocal of the catalyst weight.[4]

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(2) Mozingo, "Organic Syntheses," **21**, 15 (1941).

(3) Adams, Voorhees and Shriner, *ibid.*, **8**, 92 (1928).

(4) Smith, *et al.*, THIS JOURNAL, **67**, 272, 276 and 279 (1945).

tion. The last column indicates the "rate constants" as they have usually been calculated for a first order catalytic reaction.

Discussion

The constancy of the values of k for any given reaction indicates that equilibrium conditions were maintained in all experiments so that such factors as rate of diffusion of reaction materials to the catalyst or interference by adsorbed products were not of importance in governing the rate.

The variation in values of k' given in Table I shows that the conventional manner of treating the kinetics of heterogeneous reactions is incorrect; however, when the volume of the system is maintained constant throughout a series of reactions and comparison of conventional rate constants is made for the purpose of determining activation energies or the influence of structure on reaction velocity, no difficulty is encountered. Whenever the volume of the system is changed, or comparison of rate constants with theoretical equations is made, conventional equations are inadequate. The true rate constants for such heterogeneous reactions will differ from those for homogeneous reactions of the same order by the dimension of volume.

Similar considerations may be applied to kinetic analyses of homogeneous reactions when, for some reason or other (such as local heating) the reaction takes place only in a portion of the system.

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Summary

It has been shown that the usual method of applying kinetic equations for homogeneous reactions to heterogeneous reactions is inadequate. Whenever the volume of a gaseous system is changed, conventional rate equations must be modified. The true rate constants for such heterogeneous reactions will differ from those for homogeneous reactions of the same order by the dimensions of volume.

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[CONTRIBUTION FROM SOCONY-VACUUM LABORATORIES (A DIVISION OF SOCONY-VACUUM OIL COMPANY, INC.), RESEARCH AND DEVELOPMENT DEPARTMENT]

Kinetics of the Polymerization of Propylene with Aluminum Bromide–Hydrogen Bromide Catalyst

BY C. M. FONTANA AND G. A. KIDDER[1]

The field of olefin polymerization by means of Friedel–Crafts catalysts is old and extensive.[2] An examination of the literature, however, reveals that practically no kinetic work has appeared in the field. The present work was carried out during the winter of 1944–45 as part of a program of fundamental studies on the mechanism of the polymerization reaction using Friedel–Crafts catalysts. Aluminum bromide was chosen as a catalyst because of its relatively high solubility in hydrocarbon solvents and its known high degree of activity toward polymerization of olefins.

Early in the experimental work it was found that the rate of reaction was not reproducible when using solutions of aluminum bromide which were not anhydrous. Following the lead of similar previous experience with aluminum chloride,[2] it was soon found that promoters such as hydrogen bromide or ethyl bromide had a pronounced accelerating effect on the reaction. These findings are in line with similar findings for the aluminum bromide catalyzed isomerization of aliphatic hydrocarbons.[3,4] The rate of reaction under controlled promoter concentrations was subsequently found to be reproducible and it was also demonstrated in one experiment that no reaction occurred at low temperatures under anhydrous conditions and in the absence of added promoter. The role of the promoter was thus shown to be fundamental in the polymerization reaction and the bulk of the present work was carried out with controlled promoter concentrations.

The polymerization reaction was followed by measuring the heat evolution in terms of the volume of gas boiled from a heat insulated, constant boiling mixture surrounding the reaction flask, suitable corrections being made for heat rise in the reaction mixture and external heat losses. The heat of reaction is also obtained in terms of the heat of vaporization of the refrigerant. As far as the authors are aware the method is novel and is particularly applicable to rate studies at low temperatures. A method utilizing somewhat similar principles has been described[5] since the present work was commenced.

Experimental

Apparatus.—The apparatus used in the kinetic measurements is shown schematically in Fig. 1. The reactor was a one-liter glass flask immersed in an insulated bath which contained a fine slurry of Dry Ice–acetone. A one-gallon

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(1) Present address: The Firestone Rubber Company, Harbel Plantation, Liberia, West Africa.

(2) C. A. Thomas, "Anhydrous Aluminum Chloride in Organic Chemistry," Reinhold Publishing Corporation, New York, N. Y., 1941, Chapter 18.

(3) H. Pines and R. C. Wackher, THIS JOURNAL, 68, 595 (1946).

(4) O. Grummitt, *et al.*, *ibid.*, 67, 910 (1945).

(5) L. K. J. Tong and W. O. Kenyon, *ibid.*, 67, 1278 (1945).