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).

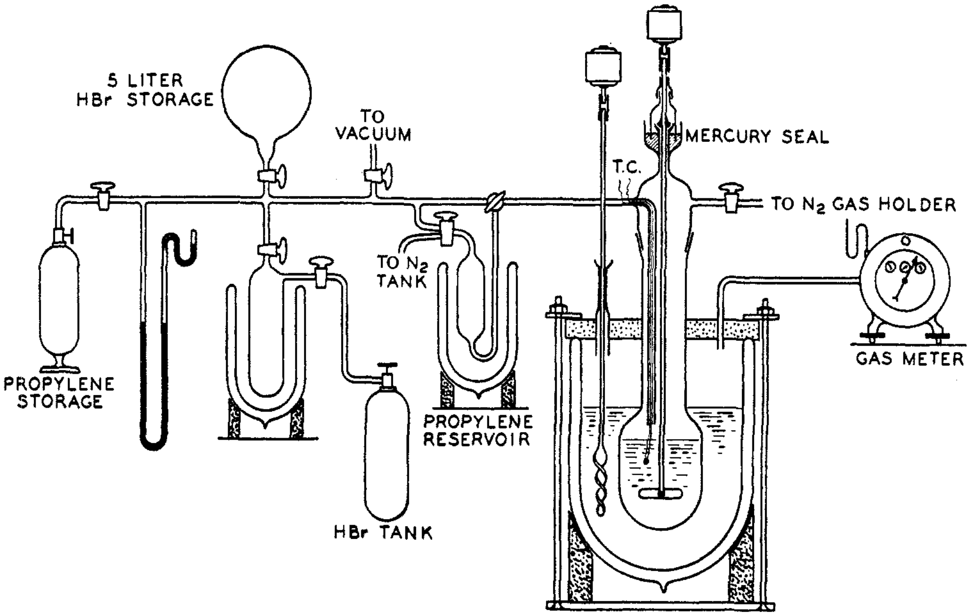


Fig. 1.—Rate measuring apparatus.

Dewar flask was used to insulate the bath and this was covered with a sheet of soft rubber one inch thick which was held in place against the Dewar by a metal ring fastened to the baseboard with four long bolts. In the later runs beginning with 9-S the Dewar flask was completely surrounded by solid Dry Ice to further eliminate heat leaks. The bath slurry was well stirred by means of a screw type impeller operated through a gas-tight ground glass sleeve. The stirring speed was high to insure equilibrium conditions in the Dry Ice–acetone-bath. The mercury seal on the reactor stirrer was provided as shown with a small ground glass spherical joint for sealing off the reactor to permit partial evacuation of the reactor when desired. In operation this spherical joint was lifted from its socket and the mercury-sealed stirrer was used in the ordinary fashion. A dry inert atmosphere was supplied to the reactor by means of a nitrogen filled gas-holder. Suitable apparatus was also provided for purifying, handling and entering the promoter and olefin at the beginning of each run. The volume of gas evolved from the bath was measured by means of a calibrated, glycerine-filled gas meter. The reactor temperature was measured by means of a copper–constantan thermocouple, inserted through the reactor entry tube, and a Leeds and Northrup type "K" potentiometer.

The general procedure for each run was to prepare an aluminum bromide solution in the normal butane solvent and assemble the surrounding Dry Ice–acetone-bath. A predetermined amount of hydrogen bromide was then introduced into the partially evacuated reactor from the storage bulb, the amount being determined from the pressure drop and the known volume of the gas system. The olefin was introduced last at the beginning of each run over a period of about fifteen seconds by pressuring the liquid olefin into the reactor from its storage bulb using tank nitrogen. Care was taken to reduce initial temperature effects to a minimum by having the liquid olefin initially at the same temperature as the reactor contents. The reaction was then followed by taking gas volume and reaction temperature readings at minute or half-minute intervals.

Reagents.—Aluminum bromide was carefully purified by several one plate distillations from bulbs containing aluminum chips and was finally purified by distillation at low pressure through a column packed with aluminum chips. In the final stages of purification the aluminum bromide was handled in an all-glass system and the white crystalline product was sealed off under vacuum into weighed ampoules for storage. Solutions of aluminum bromide in *n*-butane were made by breaking the ampoules under butane at low temperature, suitable precautions being taken to avoid exposure to air. The aluminum bromide solutions in *n*-butane were usually clear and colorless and free from insoluble matter.

The propylene used was Phillips research grade (99% min.). It was dried by passing the gas through solid potassium hydroxide and stored by condensing the gas in a small stainless steel cylinder. The propylene was entered into the system from this cylinder and measured by weight difference to about 0.1 g.

Research grade *n*-butane (99% min.) available from the pilot plant fractionators was generally used without further purification. Approximately 5 to 6 moles of butane solvent were used per run.

Commercial hydrogen bromide was degassed, given several one plate distillations to remove high boiling impurities and stored as a gas in the 5 liter bulb until used.

TABLE I

PRELIMINARY RATE DATA, POLYMERIZATION OF PROPYLENE WITH ALUMINUM BROMIDE AND VARIOUS PROMOTERS

Run no.		1-R	2-R	3-R	4-R	5-R
Concentration[a] of propylene	(Initial)	7.70	8.69	6.44	9.24	9.60
	(Final)	5.73[b]	6.35[b]	0.00	0.00	0.00
Concentration[a] of $AlBr_3$		0.20	0.20	0.20	0.20	0.20
Promoter used		None	None	EtBr	EtBr	HBr
Concn.[a] of promoter		......	......	0.20	0.22	0.49
Temperature, °C.	(Initial)	−62.0	−62.4	−62.1	−62.5	−62.3
	(Final)	−55.1	−46.5	−25.3	−27.5	−22.3
Duration, min.		20.5	60.0	20.5	48.0	< 1
Average rate (concn.[a] units per minute)		0.096	0.039	0.314	0.192	> 9.6

[a] Concentrations are expressed in moles per 100 moles of *n*-butane solvent. [b] Reaction was quenched by addition of isopropyl alcohol and the final concentration of propylene was determined by distillation analysis.

Results and Discussion

The results of some preliminary rate experiments are given in Table I. In these runs the rate was followed approximately by noting the temperature rise in a thermally insulated reactor. The results show the enormous effects of addition of promoters on the rate of the polymerization reaction. The observed slow rates in runs 1-R and 2-R are undoubtedly due to the presence of traces of extraneous promoter since the hydrocarbon reagents were not especially dried.

Following the preliminary experiments a series of runs was made in the apparatus described. In the first experiment of this series (7-S) using carefully purified and dried reagents it was found that no reaction occurred at −78.5° in the absence of added hydrogen bromide. The results of the remaining runs of the series are presented in Table II and the method of working up the raw data is illustrated for a single run (11-S) in Table III.

The general kinetic behavior of the reaction is illustrated in Fig. 2 where the rate is plotted against the time. It will be observed that the rate rises rapidly from zero, passes over a peak, flattens off rapidly and gradually falls to zero toward the end of the reaction. That the initial rise is due to an induction effect was shown experimentally by a run in which the olefin was added continuously and the addition was interrupted. When olefin addition was resumed the rate rose smoothly to a plateau (the steady state rate) with no initial peak. The results of this experiment are shown graphically in Fig. 3, where the observed rate is plotted *versus* the time.

The decrease in rate following the initial rise is associated with the appearance of a white, finely divided, solid suspension which usually precipi-

TABLE II

THE RATE DATA AND DERIVED FUNCTIONS

Time, min.	Temp., °A.	$[m]^a$	$\left(\frac{-d[m]}{dt}\right)$ (min.$^{-1}$)	$k_{TC}{}^b$	$\frac{[m]}{\left(\frac{-d[m]}{dt}\right)_0}$	$\left([m]+\frac{1}{K}\right)$
Run 8-S^c; $[AlBr_3]^a$ = 0.098, $[HBr]^a$ = 0.0866, T = 197.54						
0	194.44	9.91	0.000	0.000		
1	195.97	9.69	0.317	.422		
2	197.47	9.07	0.885	.982		
3	199.82	7.97	1.142	.970		
4	201.29	6.83	1.101	.809		
5	201.88	5.79	1.015	.720		
7	201.45	3.95	0.807	.654	8.17	5.34
9	200.05	2.58	.586	.616	6.10	3.76
11	198.65	1.59	.415	.586	4.43	2.60
13	197.54	0.89	.285	.570	3.12	1.78
15	196.67	0.42	.187	.62	1.99	1.23
17	195.97	0.13	.102	.85	1.03	0.88
19	195.32	0.02	.025			
Run 9-S; $[AlBr_3]$ = 0.163, $[HBr]$ = 0.0814, T = 200.73						
0	194.36	9.84	0.000	0.000		
1	196.01	9.83	0.181	0.367		
2	198.40	9.06	0.970	1.450		
3	201.35	7.78	1.280	1.380		
4	203.00	6.43	1.238	1.175		
5	203.36	5.30	1.084	1.023		
6	203.08	4.26	0.965	0.988	5.96	5.90
7	202.35	3.38	.826	.974	5.03	4.90
8	201.56	2.61	.707	.974	4.11	4.00
9	200.73	1.96	.592	.978	3.31	3.24
10	199.91	1.43	.489	.984	2.63	2.59
11	199.17	0.98	.393	1.01	2.03	2.05
12	198.44	.64	.304	1.04	1.56	1.63
13	197.77	.38	.235	1.18	1.10	1.30
14	197.20	.17	.153		0.86	1.03
15	196.54	.07	.079			
16	195.99	.01	.034			
Run 10-S; $[AlBr_3]$ = 0.163, $[HBr]$ = 0.0973, T = 199.20						
0	194.39	20.00	0.000	0.000		
1	196.13	19.80	0.50	0.790		
2	198.14	18.72	1.074	1.298		
3	200.06	17.55	1.118	1.065		
4	201.01	16.47	1.100	0.942		
5	201.44	15.37	1.067	.871		
6	201.63	14.30	1.035	.835		
8	201.45	12.36	0.956	.796	17.3	13.74
10	201.03	10.54	.862	.762	15.5	11.86
12	200.42	8.90	.795	.773	13.1	10.13
14	200.05	7.34	.742	.786	11.0	8.52
16	199.59	5.94	.688	.775	9.1	7.06
18	199.20	4.63	.628	.768	7.37	5.70
20	198.84	3.43	.559	.761	5.86	4.46
22	198.35	2.42	.480	.757	4.50	3.40
24	197.90	1.54	.398	.758	3.26	2.47
26	197.32	0.85	.303	.786	2.19	1.72
28	196.68	.35	.199	.914	1.26	1.16
30	196.08	.14	.107			
32	195.42	.01	.032			
Run 11-S, $[AlBr_3]$ = 0.200; $[HBr]$ = 0.0496, T = 196.72						
0	194.33	18.20	0.000	0.000		
1	195.35	18.16	0.092	0.115		
2	195.51	18.04	.211	.257		
3	196.53	17.74	.333	.374		
4	196.66	17.38	.362	.382		
5	196.88	17.02	.335	.350		
6	196.92	16.71	.306	.313		
8	196.84	16.11	.290	.301	56.3	16.94
10	196.73	15.55	.284	.298	54.9	16.36
15	196.72	14.13	.283	.299	49.9	14.94
20	196.73	12.71	.280	.298	45.4	13.52
30	196.72	9.92	.274	.296	36.2	10.73
40	196.63	7.23	.265	.294	26.9	8.03
50	196.58	4.61	.253	.302	17.9	5.40
60	196.44	2.18	.225	.314	9.34	2.94
65	196.11	1.15	.176	.310	6.02	1.86
70	195.60	0.42	.119	.313	3.04	1.10
72	195.33	.24	.075	.34	2.66	0.91
74	194.75	.12	.044			
76	194.50	.06	.018			

[a] Concentrations are expressed in moles per 100 moles *n*-butane solvent. [b] $k_{TC} = (-d[m]/dt)_0 \times (1 + K[m])/K[m]$ where $(-d[m]/dt)_0$ is the rate corrected to the average temperature indicated using an activation energy of 10.3 kcal. and K is obtained from equation (4). [c] In run 8-S the apparatus was not surrounded by solid Dry Ice.

TABLE III

EXPERIMENTAL RESULTS AND SAMPLE CALCULATIONS—RUN 11-S

Time, min.	Temp., mv.[a]	Vol. CO_2 liters[b]	Vol. E[c]	Vol. F[e]	[m][f]	Rate, $-d[m]/dt$
0	2.7478	15.190	16.17[d]	21.63	18.200	0.00
1	2.7164	15.39	16.37	21.77	18.163	.092
2	2.7116	15.77	16.90	22.23	18.042	.211
3	2.6926	16.37	18.09	23.36	17.743	.333
4	2.6762	17.32	19.55	24.75	17.376	.362
5	2.6695	18.52	20.96	26.10	17.019	.335
6	2.6682	19.73	22.21	27.28	16.707	.306
8	2.6707	22.20	24.61	29.55	16.107	.290
10	2.6742	24.57	26.87	31.68	15.547	.284
15	2.6744	30.27	32.56	37.05	14.126	.283
20	2.6743	35.96	38.25	42.41	12.709	.280
30	2.6746	47.16	49.44	52.95	9.924	.274
40	2.6773	58.08	60.28	63.14	7.232	.265
50	2.6787	68.69	70.84	73.05	4.613	.253
60	2.6832	78.70	80.71	82.27	2.177	.225
65	2.6927	83.195	84.915	86.150	1.152	.176
70	2.7089	86.810	88.023	88.933	0.417	.119
72	2.7171	87.880	88.840	89.620	.236	.0748
74	2.7256	88.722	89.414	90.064	.1184	.0438
76	2.7348	89.356	89.762	90.282	.0608	.0182
78	2.7426	89.788	89.950	90.340	.0454	...
84	2.7482	90.512	90.512	90.512	.0000	.000

[a] Millivolts on Cu–Const. thermocouple (reaction temperature: 2.7478 = −78.83°). [b] Volume of carbon dioxide measured at 28.0° and 740 mm. pressure. [c] Effective volume, corrected for temperature rise of the reaction mixture: $Vol_E = Vol\ CO_2 + 31.19\ (2.7478 - mv)$. [d] This value is corrected for the small amount of heat introduced by the liquid propylene. [e] Final corrected volume including correction for heat leak amounting to 0.065 liter of carbon dioxide per minute. [f] Concentration of propylene, $[m] = [(90.512 - Vol_F)/68.88]\ 18.20$ (moles of propylene per 100 moles of *n*-butane).

tates out of solution. On warming to room temperature this precipitate discolors and becomes a tar of the type usually obtained with Friedel–Crafts catalysts. The initial decrease in rate is thus believed to be due to removal of part of the active catalyst from the reaction by incorporation with the solid complex. The presence of this complex, whether it remains suspended or precipitates, does not seem to alter the subsequent kinetic behavior.

It should be stated at this point that the polymerization reaction is known to be essentially homogeneous since the presence of various packing materials such as porcelain, iron surface, etc., does not essentially alter the characteristics of the products. Hence it can be concluded that surface reactions do not enter into the mechanism in a fundamental way.

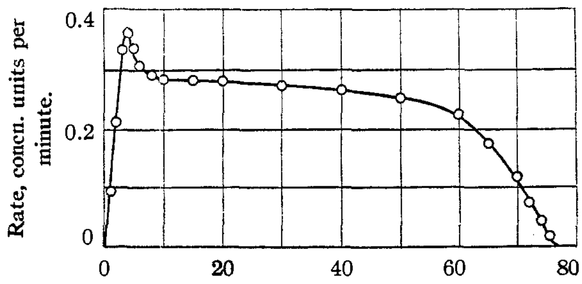


Fig. 2.—Typical rate behavior in the polymerization reaction (run 11-S).

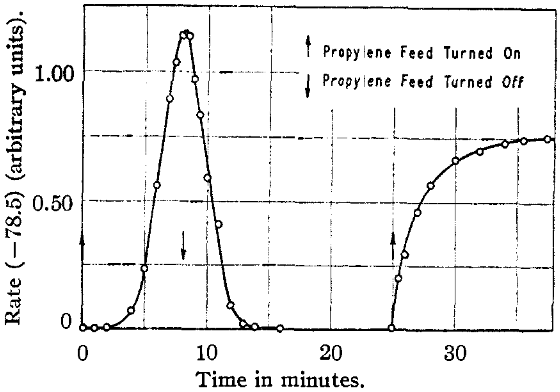


Fig. 3.—The effect of interrupting the olefin feed on the rate of propylene polymerization (experimental conditions: temp. −78.5°C., $[AlBr_3]$ = 0.163, [HBr] = 0.113, olefin feed rate = 0.227 concentration unit per minute).

Relative to the discussion that follows it should also be noted that the molecular weight of the product formed under the conditions used in these experiments is fairly high since the products are of the nature of plastic semi-solids.

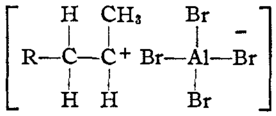
Mechanism of the Reaction.—Passing over the induction portion of the rate curve for the moment, and considering the main portion of the reaction in experiment 11-S, it will be observed that the rate is nearly constant over a large range of monomer concentration. Again, on comparison of Runs 9-S and 10-S (see Table II) where the initial concentration of propylene differed by a factor of two, the rates in the portion immediately following the peak are roughly comparable. These results lead to the conclusion that the rate here is independent of monomer concentration.

On comparison of the results of runs 11-S and 10-S and in view of the results of run 7-S it is evident that the rate in the middle portion is approximately proportional to the promoter concentration. It thus seems reasonable to assume that the rate is dependent only on the concentration of an active complex containing one molecule of hydrogen bromide and probably one molecule of aluminum bromide. Considering now the decrease in rate toward the end of the reaction, it is seen that this decrease cannot be due to an irreversible destruction of the active complex since the reaction rate is resumed on addition of more olefin. Here the rate appears to be limited by the low concentration of monomeric olefin.

A mechanism which takes into account all these observations is the following: Let us assume the existence of an associative equilibrium of the type

$$m_nc + m \overset{K}{\rightleftarrows} m_ncm \qquad (1)$$

where m_nc is a polymer–catalyst–promoter complex, and m is olefin monomer. The complex m_nc may be regarded as a carbonium ion coupled with an anion such as



$$\left[R-\overset{H}{\underset{H}{C}}-\overset{CH_3}{\underset{H}{C^+}}\ Br-\overset{Br}{\underset{Br}{Al^-}}-Br \right]$$

Let us further assume that the rate controlling step is the rearrangement of the associated monomer to form a new complex with one more unit on the polymer, *i. e.*

$$m_ncm \xrightarrow{k} m_{n+1}c \qquad (2)$$

Putting $c = \sum_n [m_nc] + \sum_n [m_ncm]$, it can be readily shown that the resulting rate equation is

$$\frac{-d[m]}{dt} = \frac{kKc[m]}{1 + K[m]} \qquad (3)$$

That equation (3) is approximately in agreement with experimental rate data is shown in Fig. 4 where the function, $m/(d(m)/dt)$, for the last portion of run 11-S is plotted against [m] to give a straight line relationship. In order to obtain a more accurate fitting of the rate data with equation (3) taking into account the variation of K and k with temperature and in order to obtain more reliable values for the constants it is necessary to obtain at least approximate values of the activation energy, ΔE, for reaction (2) and ΔH for reaction (1).

Determination of $\Delta E(2)$ and $\Delta H(1)$.—Approximate values of these quantities were obtained by comparison of the rates in an experiment (12-S, Table IV) carried out under nearly adiabatic conditions with the rates observed in the similar experiment, 11-S, carried out under nearly isothermal conditions. It was found that a reasonable agreement could be obtained between calculated and observed rates in experiment 12-S (see Table IV) on the basis of the following values of parameters: $k_{196.22}$ (rel.) = 6.04 (Table V), ΔE(2) = 10.3 kcal., $\Delta H(1)$ = 8.9 kcal., and

$$\log K = (1946/T) - 9.800 \qquad (4)$$

Also it was noted that the degree of correlation is quite sensitive to the values for $\Delta E(2)$ and $\Delta H(1)$.

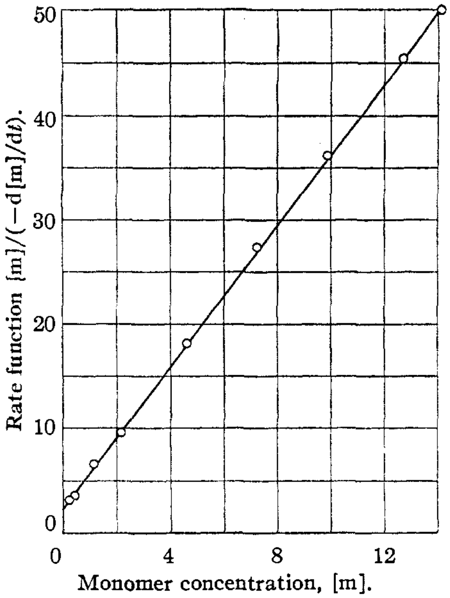


Fig. 4.—Rate function $[m]/(-d[m]/dt)$ *versus* monomer concentration [m], (run 11-S).

TABLE IV

THE RATE OF POLYMERIZATION OF PROPYLENE UNDER NEARLY ADIABATIC CONDITIONS

Run 12-S; $[AlBr_3]^a$ = 0.200, $[HBr]^a$ = 0.0481

Time min.	Temp., °A.	$[m]^a$	$\frac{d[m]}{dt}$ (min.$^{-1}$)	
			Rate, Exptl.[b]	Calcd.[c]
0	193.6	10.20	0.000	..
1	193.6	10.18	.04	..
2	194.2	9.99	.39	..
3	196.2	9.46	.69	..
4	199.5	8.62	.92	..
5	203.6	7.61	1.01	..
6	207.4	6.60	0.95	0.84
7	211.1	5.61	1.10	1.05
8	216.0	4.37	1.26	1.28
9	220.8	3.10	1.21	1.27
10	225.2	1.95	1.05	0.98
11	228.1	1.072	0.78	.59
12	230.0	0.412	.43	.25
13	230.4	0.125	.16	.08

[a] Concentrations are expressed in moles per 100 moles of n-butane solvent. [b] Experimental rates were obtained from the rate of temperature rise of the reaction mixture after suitable corrections for heat leak. [c] Calculated rates were obtained from the results of run 11-S, $k_{196.72}$(rel) = 6.04, $K_{196.72}$ = 1.23 and equation (4) assuming an activation energy of 10.3 kcal. for equation (2).

TABLE V

SUMMARY OF EXPERIMENTAL CONDITIONS AND RESULTS OF RATE EXPERIMENTS

	7-S	8-S	9-S	10-S	11-S
Initial $[m]^a$	10.00	9.91	9.84	20.00	18.20
$[AlBr_3]^a$	0.163	0.098	0.163	0.163	0.200
$[HBr]^a$	0.00	0.0866	0.0814	0.0973	0.0496
Ref. temp., Å.	194.33	197.54	200.73	199.20	196.72
ΔH,[b] kcal.	.....	......	16.6	......	16.4
k_Tc[c]	0.00	0.633	0.99	0.791	0.300
k_Tc[d] (max.)	.00	1.05	1.5	1.3	.39
$k_{196.72}c$[e]	.00	0.568	0.556	0.565	.300
$k_{196.72}c$[e](max.)	.00	0.94	0.84	0.93	.39
$k_{196.72}$(rel.)[f]	.....	6.56	6.83	5.80	6.04
$k_{196.72}$[g]	.....	10.9	10.3	9.6	7.9

[a] Concentrations are expressed in moles per 100 moles n-butane solvent. [b] Over-all heat of reaction in kcal. per mole of propylene. [c] Average value (graphical) over later portion of run at the reference temperature noted (concentration units min.$^{-1}$). [d] Approximate value from peak rate. [e] Corresponding values at a common temperature of 196.72°A. using 10.3 kcal. activation energy. [f] Relative rate constant (min.$^{-1}$) over later portion of run. [g] Approximate rate constants from peak rate.

In view of the rather limited amount of experimental material upon which these determinations are based they may be regarded as approximate and tentative. However, they should suffice for the purpose of adjusting the observed rate data from the nearly isothermal experiments in order to obtain a satisfactory comparison with theory and in order to evaluate constants.

The Induction Reaction.—The general form of the initial rate rise is similar to that observed for autocatalytic reactions. A possible mechanism for the induction is thus

$$m_ncm + c' \xrightarrow{k} m_nc + mc' \qquad (5)$$

where c' is probably hydrogen bromide and mc' is rapidly converted to mc by reaction with aluminum bromide. According to this reaction the maximum rate of formation of active complex should be approximately proportional to the square of the initial promoter concentration and this is approximately in accordance with the experimental data.

Correlation of Experimental Results.—By use of equation (4) to determine K and using an activation energy of 10.3 kcal., the function, $(1 + K[\mathrm{m}]/K[\mathrm{m}] \times (-\mathrm{d}[\mathrm{m}]/\mathrm{d}t)_0$, can be examined for constancy. The degree of constancy obtained in these portions of the runs following the initial peak is indicated in Table II. The agreement between theory and experiment is perhaps best shown on a plot of $[\mathrm{m}]/(-\mathrm{d}[\mathrm{m}]/\mathrm{d}t)_0$ *versus* $([\mathrm{m}] + 1/K)$ as in Fig. 5. Values of these functions are given in Table II and a schematic potential energy diagram of the mechanism entailed is depicted in Fig. 6.

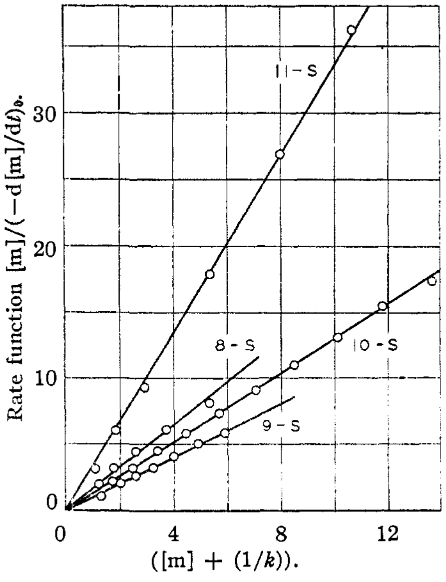


Fig. 5.—Correlation of theory and experiment (theory, straight lines through origin).

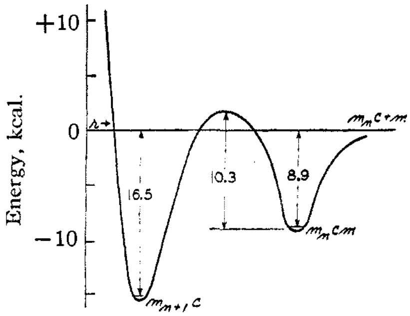


Fig. 6.—Schematic potential energy diagram for the polymerization of propylene with aluminum bromide–hydrogen bromide catalyst.

When values of $k_{\mathrm{T}C}$ are plotted *versus* time for the initial portion of each run as in Fig. 7, maximum values, $k_{\mathrm{T}C}$(max.), may be determined. If these maximum values represent conditions under which essentially all the original catalyst-promoter is effective, they may be used for determining the approximate rate constants, k_{T}. A summary of the experimental conditions and results of the rate experiments appears in Table V.

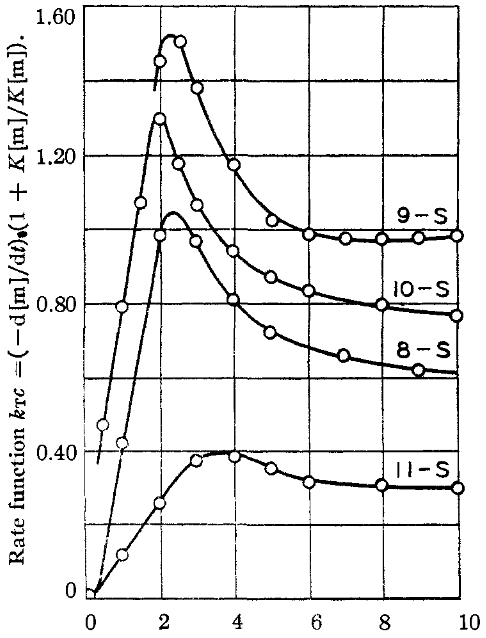


Fig. 7.—Initial portions of rate function $(-\mathrm{d}m/\mathrm{d}t)_0 \cdot (1 + k\,[\mathrm{m}]/k[\mathrm{m}])$ *versus* time.

In accordance with the postulated mechanism herein presented it is seen that the polymerization reaction follows essentially a definite stepwise synthesis of the polymer product rather than a normal chain reaction mechanism wherein the chain is initiated, is rapidly built up and then terminated by a catalyst destruction or chain transfer reaction. This conclusion is in agreement with an observed steady rise in the product viscosity during the initial stages of the polymerization reaction and with the very low viscosity value observed when the viscosity curve is extrapolated to zero time.

The mechanism postulated is incomplete in that no mention has been made of a chain transfer or chain termination step although at least one such step is known to be present since the molecular weight of the product does not increase indefinitely with the amount of olefin polymerized. The presence of such a step (provided there is no appreciable amount of catalyst destruction) would have no observable effect on the results of the present kinetic study.

Summary

1. The kinetics of the polymerization of propylene by means of aluminum bromide in the presence of hydrogen bromide promoter have been investigated.

2. A mechanism which accounts for the experimental data has been proposed.

3. Approximate values of a rate constant, an equilibrium constant and the corresponding activation and heat energies have been determined.

4. The heat of polymerization of propylene has been found to be approximately 16.5 kcal. per mole.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF TEXAS]

Molybdenum(III) Oxide[1]

BY GEORGE W. WATT AND DARWIN D. DAVIES[2]

Although several methods for the formation of molybdenum(III) oxide hydrates have been described,[3] there is no satisfactory procedure for the direct production of the anhydrous oxide. The method of Wherry and Smith[4] yields pure molybdenum(II) oxide 3-hydrate; the same product in less pure form is afforded by the method of Berzelius.[5]

In the course of certain work on the reduction of molybdenum(VI) oxide by means of solutions of potassium in liquid ammonia, it has been found that anhydrous molybdenum(III) oxide may be formed in accordance with the equation

$$2MoO_3 + 6K + 3NH_3 \longrightarrow Mo_2O_3 + 3KOH + 3KNH_2$$

Upon completion of the reduction reaction, the oxide is purified by treatment with ammonium bromide followed by washing with liquid ammonia at least ten times. Experiments described below show that the oxide thus prepared and purified forms a 3-hydrate identical with that prepared by the method of Wherry and Smith.[4] In the course of this work it was shown also that commercial products purported to be molybdenum(III) oxide consist principally of molybdenum(IV) oxide and molybdenum.

Experimental

Materials.—Molybdenum(VI) oxide was prepared as described previously.[6] Samples prepared by different methods and treated differently prior to use gave identical results. All of the other chemicals employed were of reagent grade.

Methods.—Equipment and procedures for the conduct of the reduction reactions in liquid ammonia at its normal boiling point and under anhydrous conditions were essentially identical with those described by Watt and Moore.[7]

Preparation of Molybdenum(III) Oxide.—Small samples of molybdenum(VI) oxide (0.3–0.7 g.) in 20–25 ml. of anhydrous liquid ammonia[8] were reduced by addition of quantities of potassium slightly in excess of 3 equivalents. Typical data relative to these reactions are given in Table I. That the reduction is substantially quantita-

TABLE I

PREPARATION OF MOLYBDENUM(III) OXIDE

MoO_3, g.	K g.	K equiv.	H_2, cc. at 0°, 760 mm.	NH_4Br, g.	Ratio[a] K/ MoO_3	Mo,[b] %
0.5205	0.4430	3.13	5.5	None	3.00	78.85
.5250	.4425	3.10	4.2	None	3.00	78.78
.6522	.5511	3.11	5.6	0.6200	2.99	79.82
.5650	.4720	3.08	2.9	.5120	3.01	79.90
.6006[c]	.5131	3.15	7.2	.5080	2.99	79.83
.4999[c]	.4281	3.15	3.0	1.0021	3.08	79.71

[a] Calculated in terms of molybdenum(VI) oxide used and the total potassium added less that equivalent to the quantity of hydrogen collected. [b] Calcd. for Mo_2O_3: Mo, 79.99. In addition to analyses for molybdenum, each insoluble product was analyzed for nitrogen and potassium. For runs in which ammonium bromide was not added, the results were: N, 0.72 ± 0.03; K, 2.99 ± 0.16. When ammonium bromide was added, the results were: N, 0.52 ± 0.09; K, 0.58 ± 0.08. These data reflect the improvement in purity resulting from treatment with ammonium bromide, but show also that this treatment together with at least 10 washings with liquid ammonia fails to remove these impurities completely. The analytical values for molybdenum bespeak a degree of purity that is incompatible with the analytical values for nitrogen and potassium. However, the method employed in analyses for molybdenum was carefully checked using samples of known purity and it is believed that the molybdenum analyses are the most reliable. Also, there were present in the molybdenum(III) oxide no impurities detectable by means of X-ray diffraction patterns. [c] These experiments are typical of cases in which the oxide was added to a solution of potassium, *i.e.*, a reversal of the more usual order of addition of reactants.

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[1] This work was supported in part by The University Research Institute, Project No. 25.

[2] Present address: The General Electric Co., Richland, Washington.

[3] Mellor, "A Comprehensive Treatise on Inorganic and Theoretical Chemistry," Longmans, Green and Co., New York, N. Y., 1931, Vol. XI, p. 525.

[4] Wherry and Smith, THIS JOURNAL, **29**, 806 (1907).

[5] Berzelius, *Pogg. Ann.*, **7**, 261 (1826).

[6] Watt and Davies, THIS JOURNAL, **70**, 2041 (1948).

[7] Watt and Moore, *ibid.*, **70**, 1197 (1948).

[8] Although it has been shown that molybdenum(VI) oxide reacts with liquid ammonia to form a 3-ammoniate that may be interpreted as a diammonium aquoammonomolybdate,[9] its behavior upon reduction with potassium is not typical of ammonium salts. The molecular hydrogen liberated during the course of the reduction reactions was only that equivalent to the excess potassium added.