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Chain Transfer of Vinyl Monomers with Carbon Tetrabromide[1,2]

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The chain transfer constants of six vinyl monomers with carbon tetrabromide have been measured at several temperatures. The monomers employed, in the order of their decreasing transfer constant at 60° are: vinyl acetate, *p*-chlorostyrene, styrene, methyl acrylate, methyl methacrylate and methacrylonitrile. Since the propagation rate constants for all but one of these monomers have been independently measured, the rate constants for the transfer step with carbon tetrabromide have been calculated and the frequency factor and activation energy values tabulated wherever possible. The results indicate that ionic forms in the transition state, similar to those involved in radical addition to double bonds, contribute to the reactivity of radicals in transfer reactions. Extending the Alfrey–Price *Q*,*e* scheme for copolymerization reactions to chain transfer reactions, it is possible to calculate *Q* and *e* values for carbon tetrabromide and thereby anticipate the transfer constant of any monomer with this reagent for which the *Q* and *e* values have been determined by copolymerization studies. A relationship between intrinsic viscosity and number average molecular weight is reported for three unfractionated polymers, *p*-chlorostyrene, methyl acrylate and methacrylonitrile.

Chain transfer measurements have been employed by several investigators[3-8] to study the reactivity of organic molecules with substituted ethylenic radicals. The reactions under consideration are of the type

$$RM\cdot_n + M \xrightarrow{k_p} RM\cdot_{n+1} \qquad (1)$$

$$RM\cdot_n + SX \xrightarrow{k_{tr}} RM_nX + S\cdot \qquad (2)$$

where $RM\cdot_n$ represents a polymer radical which may either continue growth by addition of a monomer, M, or react with a transfer reagent, SX, having a displaceable atom, X, to yield a dead polymer molecule, RM_nX, and the radical, $S\cdot$. The experimentally measurable transfer constant C, is the ratio of the specific rate constants for propagation, k_p, and transfer, k_{tr} (*i.e.*, $C = k_{tr}/k_p$).

Investigations of the relative reactivity of vinyl monomers in copolymerization reactions have clearly demonstrated the importance of polar and resonance factors in determining the addition of radicals to ethylenic double bonds.[9,10] In the course of evaluating the application of radioactive tracer methods to the measurement of the transfer constants of vinyl monomers with *n*-butyl mercaptan, Walling[6] has suggested that polar and resonance factors are also involved in chain transfer reactions. These factors are discussed in greater detail in the review article of Mayo and Walling[11] and have also been considered by Gregg and Mayo[3f] in evaluating the transfer reactivities of a number of organic compounds with styrene. In the present work, which supports the conclusions of the above-mentioned investigators, the transfer constants of six vinyl monomers with carbon tetrabromide were determined by conventional procedure involving molecular weight determinations from viscosity or osmotic pressure measurements. Carbon tetrabromide was chosen in this investigation since there is no ambiguity concerning the atom involved in the transfer reaction. In addition, this reagent exhibits no appreciable retarding influence on polymerization rate and its high reactivity enables precise measurement of transfer constants.

Experimental

Purification of Materials.—Methyl methacrylate (Rohm and Haas) was vacuum distilled from inhibitor: b.p. 46–47° (100 mm.), $n^{25}D$ 1.412.

Styrene (The Dow Chemical Co.) was separated from inhibitor by vacuum distillation under nitrogen: b.p. 70–71° (61 mm.), $n^{24.5}D$ 1.5441.

Vinyl acetate (Eastman Kodak Co.) was used freshly distilled from inhibitor at atmospheric pressure; b.p. 72.5°, $n^{20}D$ 1.3958.

Methyl acrylate (Eastman Kodak Co.) was vacuum distilled from inhibitor: b.p. 50° (246 mm.), $n^{20}D$ 1.4025.

Methacrylonitrile (Shell Development Co.) was vacuum distilled from inhibitor under nitrogen: b.p. 37.5° (100 mm.), $n^{20}D$ 1.4007.

p-Chlorostyrene (Monomer–Polymer, Inc.) was vacuum distilled from inhibitor: b.p. 69–70° (8 mm.), $n^{25}D$ 1.564.

The reagents benzene, acetonitrile, carbon tetrachloride, dimethylformamide (b.p. 151–152°) and carbon tetrabromide were of highest available purity and were used as received from freshly opened bottles. The catalyst 2,2'-azobisisobutyronitrile (m.p. 103–104°) was prepared and purified according to the method of Overberger, O'Shaughnessy and Shalit[12] as adapted from the procedure of Thiele and Heuser.[13]

Polymerization of Monomers.—All polymerization reactions were performed in solution using benzene, acetonitrile or dimethylformamide as solvent. The following procedure described for methyl acrylate polymerization was employed, with only minor exceptions, for each of the other monomers. Into a clean Pyrex tube was pipetted a portion of a benzene solution of carbon tetrabromide, 10 ml. of methyl acrylate, 1 ml. of a benzene solution of the azobisisobutyronitrile catalyst and lastly, sufficient benzene to yield a total volume of 15 ml. (all volumes measured at 20°). The contents of the tubes were frozen with liquid nitrogen and degassed in a high vacuum line. The contents were subjected to repeated thawing and freezing operations to

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[2] Taken in part from the dissertation of Nathan Fuhrman, submitted in March, 1953, in partial fulfillment of the requirements for the Ph.D. degree. This paper was presented before the Division of Polymer Chemistry at the 124th Meeting of the American Chemical Society in Chicago, Ill., September, 1953.

[3] (a) F. R. Mayo, THIS JOURNAL, **65**, 2324 (1943); (b) R. A. Gregg and F. R. Mayo, *Faraday Soc. Disc.*, **2**, 328 (1947); (c) R. A. Gregg and F. R. Mayo, THIS JOURNAL, **70**, 2373 (1948); (d) F. R. Mayo, *ibid.*, **70**, 3689 (1948); (e) R. A. Gregg, D. M. Alderman and F. R. Mayo, *ibid.*, **70**, 3740 (1948); (f) R. A. Gregg and F. R. Mayo, *ibid.*, **75**, 3530 (1953).

[4] G. M. Burnett and H. W. Melville, *Faraday Soc. Disc.*, **2**, 322 (1947).

[5] C. H. Bamford and M. J. S. Dewar, *ibid.*, **2**, 314 (1947).

[6] C. Walling, THIS JOURNAL, **70**, 2561 (1948).

[7] (a) S. Basu, J. N. Sen and S. R. Palit, *Proc. Royal Soc.* (*London*), **A202**, 485 (1950); (b) **A214**, 247 (1952).

[8] S. L. Kapur, *J. Polymer Sci.*, **11**, 399 (1953).

[9] F. R. Mayo and C. Walling, *Chem. Revs.*, **46**, 191 (1950).

[10] T. Alfrey, J. J. Boherer and H. Mark, "Copolymerization," Interscience Publishers, Inc., New York, N. Y., Chapters III–V, 1952.

[11] Reference 9, pp. 264–270.

[12] C. G. Overberger, M. T. O'Shaughnessy and H. Shalit, THIS JOURNAL, **71**, 2661 (1949).

[13] J. Thiele and C. Heuser, *Ann.*, **290**, 1 (1896).

remove dissolved gases. The tubes were then sealed *in vacuo* below 10^{-4} mm. and immediately subjected to polymerization in a constant temperature bath to less than 10% conversion. The polymerization times at each temperature were predetermined by trial experiments.

Purification of Polymers.—The procedures employed for the purification of styrene, *p*-chlorostyrene, methyl methacrylate and methacrylonitrile polymers were identical. The tubes on removal from the polymerization bath were rapidly cooled in Dry Ice before opening at room temperature. The contents were transferred to a 60-ml. separatory funnel and diluted twofold with acetone, in the case of polymethyl methacrylate and polymethacrylonitrile, and with butanone in the case of polystyrene and poly-*p*-chlorostyrene. The polymer solutions were added dropwise to a large volume of continuously agitated methanol. The volume ratio of polymer solution to non-solvent was approximately 1:12. All four polymers were precipitated in the form of finely divided particles and were easily collected on fritted glass filters. After several washings with methanol the samples were dried overnight *in vacuo* at 50°. Whereas successive precipitations were not found necessary for viscosity measurements, the samples employed for osmotic pressure studies were subjected to two additional precipitations.

Polyvinyl acetate was precipitated from the polymerized reaction mixture according to the procedure of Alfrey and Berdick.[14] Petroleum ether (boiling range 30–60°) was used in place of *n*-hexane recommended by these authors. The polymer was dried overnight *in vacuo* at room temperature.

Polymethyl acrylate was purified by precipitation into petroleum ether (boiling range 30–60°) from a polymer solution diluted with ethyl acetate. The volume ratio of polymer solution to non-solvent was 1:13. In order to prevent the polymer from settling in the form of a gummy solid it was necessary to employ vigorous stirring and to cool the petroleum ether to −50°. The finely divided precipitate was rapidly collected on a fritted glass filter and washed with cold petroleum ether. At no time was the polymer allowed to warm above its second-order transition point of 3°. The polymer was immediately placed in a vacuum desiccator, previously cooled and packed in Dry Ice, and kept under vacuum for six hours. Evacuation of the samples was further continued for at least 12 hours at room temperature. The polymer was then subjected to two successive precipitations from ethyl acetate solution into petroleum ether using the same procedure as described above.

Osmotic Pressure Measurements.—Osmotic pressure studies were performed with Zimm-Myerson[15] glass osmometers using conditioned membranes of wet regenerated cellophane, type 300 obtained from the Sylvania Division of the American Viscose Corporation. The osmotic pressures at 25° were determined at four polymer concentrations between 0.1 and 1.0 g./100 ml. solvent using the static method.

TABLE I

CATALYZED POLYMERIZATION OF MONOMERS IN THE PRESENCE OF CARBON TETRABROMIDE

$[CBr_4]^a \times 10^4$ / [Monomer]	[Catalyst] $\times 10^3$, mole/liter	Polym. temp., °C.	Time, hr.	Conversion, %	$[\eta]$, cm.^{3}/g.	$\bar{P}_n$,[b] (osmotic)	$1/\bar{P}_n \times 10$ $[\eta]^c$
Experiments with styrene in benzene solvent							
0.875	7.2	40	19	5.7	90.2		8.85
1.75	7.2	40	19	5.5	79.5		10.6
3.50	7.2	40	19	5.5	66.0		13.6
5.25	7.2	40	19	5.1	56.8		16.7
7.00	7.2	40	19	5.0	50.0		19.9
0.875	1.0	60	6.0	5.3	84.5		9.66
1.00	1.0	60	6.0	5.1	83		9.93
1.25	1.0	60	6.0	5.2	80		10.4
2.50	1.0	60	6.0	5.1	67		13.3
3.00	1.0	60	6.0	4.9	62		14.8
3.75	1.0	60	6.0	4.9	58		16.2
5.00	1.0	60	6.0	4.7	52		18.8
5.00	1.0	60	6.0	4.6	52		18.8
1.50	0.38	80	2.0	6.0	70.2		12.5
3.00	.38	80	2.0	5.7	58.0		16.3
4.50	.38	80	2.0	5.6	50.6		19.6
6.00	.38	80	2.0	5.4	44.3		23.4
Experiments with styrene in acetonitrile solvent							
1.25	1.0	60	6.0	4.7	69.0		12.8
2.50	1.0	60	6.0	4.6	59.2		15.8
3.75	1.0	60	6.0	4.5	52.0		18.9
5.00	1.0	60	6.0	4.4	45.8		22.4
Experiments with methyl methacrylate in benzene solvent							
0.0	10	60	0.5	6.0	143		3.61[d]
10.0	10	60	.5	5.9	100		7.64
30.0	10	60	.5	5.8	63		13.6
50.0	10	60	.5	5.4	50		18.2
70.0	10	60	.5	5.4	41		23.3
0.0	0.30	80	.5	5.9	241		1.88[d]
10.0	.30	80	.5	5.7	120		6.08
30.0	.30	80	.5	5.5	69		12.1
50.0	.30	80	.5	5.0	48		19.1
0.0	.041	100	1.0	5.9	296		1.46[d]
10.0	.041	100	1.0	5.5	112		6.62
20.0	.041	100	1.0	5.3	75		11.0
30.0	.041	100	1.0	5.0	56		15.8
Experiments with methyl acrylate in benzene solvent							
5.0	1.4	40	4.2	4.4	133		2.30
5.0	1.4	40	6.7	4.3	124		2.50
10.0	1.4	40	6.7	8.2	79.6	2380	4.31
15.0	1.4	40	5.8	5.2	59.0	1670	6.21
20.0	1.4	40	5.8	5.9	49.2	1325	7.75
5.0	0.26	50	3.05	8.9	115	3630	2.73
5.0	.26	50	2.0	8.7	117		2.69
10.0	.26	50	3.05	4.3	66.4		5.35
15.0	.26	50	3.05	3.8	57.0		6.46
20.0	.26	50	3.05	2.2	47.4		8.07
5.0	.050	60	4.0	7.3	105		3.07
5.0	.050	60	4.8	1.2	103		3.15
10.0	.050	60	4.8	7.8	69.0	1790	5.12
15.0	.050	60	4.8	1.9	51.0		7.41
20.0	.050	60	4.8	4.9	42.0		9.39
Experiments with methacrylonitrile[e] in dimethylformamide solvent							
10.0		100	44	4.9	140	7240	1.43
20.0		100	44	6.3	108	3980	2.28
30.0		100	44	6.0	90.0	2890	3.18
40.0		100	44	7.0	76.5	2690	4.27
10.0		120	17.5	7.6	109		2.26
20.0		120	17.5	10.2	88		3.31
30.0		120	17.5	10.7	75		4.42
40.0		120	17.5	11.9	66		5.56
Experiments with vinyl acetate in benzene solvent							
0.000	1.0	60	3.5	3.2	119		4.84
.010	1.0	60	3.5	2.9	113		5.18
.020	1.0	60	3.5	2.4	107		5.62
Experiments with *p*-chlorostyrene in benzene solvent							
0.50	1.0	60	4.5	6.0	43.7	888	11.2
1.00	1.0	60	4.5	5.8	37.0	721	13.8
1.50	1.0	60	4.5	5.7	32.5	606	16.3
2.00	1.0	60	4.5	5.6	28.7		19.1

[a] Initial molar carbon tetrabromide to monomer ratios. [b] From osmotic pressure studies. [c] Calculated from the appropriate equation in equations 3–8. [d] Determined from the equation $\bar{P}_n = 5.61\ [\eta]^{1.25}$, reference 17. [e] Thermal polymerization.

The experimental conditions employed in the preparation of polymethyl acrylate, polymethacrylonitrile and poly-*p*-chlorostyrene samples for osmotic pressure studies are given in Table I along with the measured values of $\bar{P}_n$ (osmotic).

Determination of Degrees of Polymerization. Limiting Viscosity Number Relationships.—Solution viscosities of the polymer samples were determined with the aid of an Ubbelohde dilution viscometer having flow times of 105 seconds for chloroform at 20°, 110 seconds for acetone at 20° and 180 seconds for benzene at 30°. At these flow times kinetic energy corrections are not required. Acetone was employed as the solvent for polymethyl acrylate, polyvinyl acetate and polymethacrylonitrile, chloroform for poly-

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(14) T. Alfrey and M. Berdick, *J. Polymer Sci.*, **3**, 899 (1948).

(15) B. H. Zimm and I. Myerson, THIS JOURNAL, **68**, 911 (1946).

methyl methacrylate and benzene for polystyrene and poly-*p*-chlorostyrene. The limiting viscosity numbers of the unfractionated polymers were obtained from the viscosity numbers at four or more polymer concentrations.

The number average degrees of polymerization ($\bar{P}_n$) of the various polymer samples were calculated from viscosity relationships established in the present work or by other investigators.

The following relationships were employed

Polymethyl acrylate	$\bar{P}_n = 11.2\ [\eta]^{1.22}$ at 20°	(3)
Polymethacrylonitrile	$\bar{P}_n = 0.92[\eta]^{1.81}$ at 20°	(4)
Poly-*p*-chlorostyrene	$\bar{P}_n = 6.9\ [\eta]^{1.29}$ at 20°	(5)
Polymethyl methacrylate	$\bar{P}_n = 4.15[\eta]^{1.25}$ at 20°	(6)
Polystyrene	$\bar{P}_n = 2.37[\eta]^{1.37}$ at 30°	(7)
Polyvinyl acetate[16]	$\bar{P}_n = 2.57[\eta]^{1.40}$ at 25°	(8)

The limiting viscosity number $[\eta]$ appearing in equations 3–8 is in the units of cm.^{3} per gram. Each of the above relationships was calculated or determined for unfractionated polymer chains initiated by a monoradical source and terminated by chain transfer. Equations 3–5 were determined in the present work by evaluating, by the method of least squares, the slope and intercept of the plot of log $[\eta]$ *vs.* log $\bar{P}_n$. Molecular weight relationship for polymethyl methacrylate and polystyrene have been reported by Baysal and Tobolsky[17] and Bawn and co-workers,[18] respectively. These relationships were not established for unfractionated polymer terminated by chain transfer. However, using the method discussed by Baysal and Tobolsky[17] to relate viscosity relationships with molecular weight distributions, it was possible to calculate equations 6 and 7 from the reported data.

Viscosity–molecular weight relationships have been reported for fractionated samples of polymethyl acrylate[19] and polymethacrylonitrile.[20] However, when these relationships are adjusted[17] to unfractionated polymer chains terminated by chain transfer (disproportionation), molecular weights are obtained which deviate as much as 30% from our values.

TABLE II

CHAIN TRANSFER CONSTANTS[a] OF VINYL MONOMERS WITH CARBON TETRABROMIDE

Monomer	Transfer constant 40°	50°	60°	80°	100°	120°
Vinyl acetate			>39			
p-Chlorostyrene			5.2 ± 0.4			
Styrene[b]	1.8 ± 0.2		2.2 ± 0.2 (2.5[c])	2.3 ± 0.2		
Methyl acrylate	0.35 ± 0.2	0.35 ± 0.02	0.41 ± 0.01			
Methyl methacrylate			0.27 ± 0.02	0.33 ± 0.02	0.46 ± 0.02	
Methacrylonitrile[d]					0.09 ± 0.01	0.10 ± 0.01

[a] Estimated possible errors based on duplicate runs. The estimated errors do not take into account the accuracy of the viscosity–molecular weight relationship employed. [b] Other values reported in the literature for the transfer constant of styrene and carbon tetrabromide at 60° are as follows: C. H. Bamford and M. J. S. Dewar, ref. 5 (*C* 2.7); J. W. Breitenbach and H. Karlinger, *Monatsh.*, **82**, 245 (1951) (*C* 2–5 at 70°); and R. A. Gregg and F. R. Mayo, ref. 3f (*C* 1.36). [c] Transfer studies run in acetonitrile solvent in place of benzene. [d] Transfer studies run in dimethylformamide solvent with thermal initiation of polymerization.

Results and Discussion

Determination of Transfer Constants.—The calculations of transfer constants are based upon the equation derived by Mayo[3a]

$$1/\bar{P}_n = C[\mathrm{SX}]/[\mathrm{M}] + 1/\bar{P}_{n,0} \qquad (9)$$

where $\bar{P}_{n,0}$ is the number average degree of polymerization of polymer prepared in the absence of [SX] and is a function of monomer and catalyst concentrations, and $\bar{P}_n$ is the number average degree of polymerization of polymer prepared at a given [SX]/[M] ratio. If the concentrations of monomer and catalyst are maintained constant, *C* is the slope of the line obtained by plotting $1/\bar{P}_n$ *vs.* [SX]/[M]. In the present work the concentration ratio of [SX]/[M] was varied, while maintaining the concentration of both monomer and catalyst essentially constant, by conducting the polymerizations in the presence of an inert solvent such as benzene to low degrees of conversion. The use of solvents such as acetonitrile in styrene polymerization and dimethylformamide in methacrylonitrile polymerization also has been found satisfactory.

The transfer data obtained with the six vinyl monomers at several temperatures are presented in Table I. In all cases plots of $1/\bar{P}_n$ against $[\mathrm{CBr_4}]/[\mathrm{M}]$ gave straight lines as predicted by theory (eq. 9). Calculations of the transfer constants have been made by the method of least squares and the values are listed in Table II. Since in all the runs both the monomer and carbon tetrabromide concentrations decrease significantly, the average carbon tetrabromide:monomer ratios have been used in the calculations.

The transfer constant listed for vinyl acetate at 60° is considered to be in great error. The value of 39 is minimal and the actual value may be closer to 200 based on the relative ratios of the transfer constants of other reagents with styrene and vinyl acetate.[15] The observed low value is due to the rapid consumption of the carbon tetrabromide during reaction and, as indicated by Walling,[6] experiments generally should not be carried out to extents of reaction greater than the reciprocal of the anticipated transfer constant of the system. In this case, assuming a value of $C = 200$ the reaction should be kept below 0.5% conversion which is not experimentally practicable.

The transfer studies with methacrylonitrile were run in dimethylformamide solvent rather than benzene since the polymer is insoluble in its own monomer or in mixtures containing benzene. Although it might be assumed that the polar character of the solvent can influence the transfer constant value, it is noted in Table II that the transfer constants of styrene at 60° are essentially unchanged for reactions carried out in benzene or

[16] W. H. Stockmayer, private communication to the authors.

[17] B. Baysal and A. V. Tobolsky, *J. Polymer Sci.*, **9**, 171 (1952).

[18] C. E. H. Bawn, R. F. J. Freeman and A. R. Kamalidden, *Trans. Faraday Soc.*, **46**, 1107 (1950).

[19] H. Staudinger and K. Warth, *J. prakt. Chem.*, **155**, 261 (1940).

[20] W. Kern and H. Fernow, *ibid.*, **160**, 302 (1942).

TABLE III

PROPAGATION AND TRANSFER RATE CONSTANTS

Monomer	Q^a	k_p at 60° l. m.$^{-1}$ sec.$^{-1}$	k_{tr} at 60° l. m.$^{-1}$ sec.$^{-1}$	$A_{tr}{}^b \times 10^{-8}$	$\frac{A_{tr}{}^b}{A_p}$	E_{tr}, kcal.	$E_{tr} - E_p$,^{b} kcal.
CH_2=C—CH_3 CN	1.5	21^c	(1.05 at 30°)^d		1.04		1.8
CH_2=C—H C_6H_5	1.0	176^e	388	5.2	23.6	9.3	1.5
CH_2=C—CH_3 $COOCH_3$	0.74	367^f	99	3.1	60.7	9.9	3.6
CH_2=C—H $COOCH_3$	.42	2090^g	856	1.0	1.0	7.8	0.7
CH_2=C—H $OCOCH_3$	.01	3700^h	>144,000				

[a] Values taken from reference 22. [b] Calculated from the Arrhenius equation $C = A \exp(-E/RT)$ where $A = A_{tr}/A_p$ and $E = E_{tr} - E_p$. Values for C are given in Table II, and values for A_p and E_p appear in footnotes *e*-*g*. [c] Measured at one temperature (30°); A. Copperman, Ph.D. dissertation submitted to the Chemistry Department of the Polytechnic Institute of Brooklyn, June, 1952. A. Copperman and M. T. O'Shaughnessy paper presented at the Polymer Division of the 122nd Meeting of the American Chemical Society at Atlantic City, N. J., September 16, 1952. [d] Extrapolated from data at higher temperatures using the Arrhenius expression. [e] $k_p = 2.2 \times 10^7 \exp(-7{,}800/RT)$; M. S. Matheson, *et al.*, THIS JOURNAL, **73**, 1700 (1951). [f] $k_p = 5.1 \times 10^6 \exp(-6{,}300/RT)$; M. S. Matheson, *et al.*, *ibid.*, **71**, 497 (1949). [g] $k_p = 1 \times 10^8 \exp(-7{,}800/RT)$; M. S. Matheson, *et al.*, **73**, 5395 (1951). [h] $k_p = 2.4 \times 10^8 \exp(-7{,}300/RT)$; M. S. Matheson, *et al.*, *ibid.*, **71**, 2610 (1949).

acetonitrile solvents having dielectric constants of 2.3 and 38.8, respectively.

The radical initiated polymerization of methacrylonitrile is relatively slow compared with the other vinyl monomers and for this reason the transfer studies were carried out at 100° and 120° using thermal initiation of polymerization. Apparently the system contained sufficient adventitious catalyst to effect polymerization.[21] Polymerizations at lower temperatures using catalysts such as 2-azobisisobutyronitrile are not practical with this monomer since the reaction would have to be carried out at extremely slow rates of polymerization to produce a polymer having an appreciably high molecular weight.

Comparison of Monomers.—Since the propagation rate constants, k_p, of all the monomers listed in Table II except *p*-chlorostyrene are reported in the literature, it is possible to present a comparison of the specific rate constants for transfer, k_{tr}, of the monomers. The values of k_{tr}, calculated from the simple relation $k_{tr} = Ck_p$, are listed in Table III along with the corresponding values of A_{tr}, E_{tr}, A_p and E_p, the frequency factor for the transfer step, the activation energy for the transfer step, the frequency factor for propagation, and the activation energy for propagation, respectively. The k_{tr} value for vinyl acetate is included despite its inaccuracy since the experimental value is minimal but nevertheless appears as the highest k_{tr} value of all the monomers.

The monomers are listed in Table III in the order of their decreasing general reactivity as determined by copolymerization studies at 60°. Numerical values for the general monomer reactivity (the Q values in column 2) have been compiled by Price.[22]

Matheson and co-workers[23] have demonstrated that the propagation rate constants increase as the general monomer reactivities decrease.[24] The k_{tr} values, on the other hand, do not follow any such direct relationship since methyl methacrylate, exhibiting a k_{tr} value considerably less than that of styrene, appears completely out of line. This point will be discussed further in the succeeding section.

In column 5 of Table III are listed the frequency factors for the transfer step along with the ratio of this value to the frequency factor for propagation given in column 6. It is noted that the frequency factors for both the transfer and propagation steps (see footnotes *e-g* in Table III) are lower than the normal collision frequency factor for bimolecular reactions by a factor of 10^3 or more, while the ratio of frequency factors (A_{tr}/A_p) are not far from unity. The low A_p value for vinyl polymerization has been attributed[23,25] to the unfavorable entropy change for propagation since the monomer molecule on entering the growing chain loses several degrees of freedom. Since the frequency factor for the transfer step does not differ significantly from that for propagation, it appears that considerable restrictions in motion are imposed upon the carbon tetrabromide molecule on passing from the free state to the transition state.

Application of Chain Transfer Data to the Alfrey–Price Q,e Scheme.—It was noted previously that while k_p and Q exhibit an inverse relationship, a similar uniform relation between these quantities and k_{tr} does not exist. In particular, it may be seen in Table III that only in the case of styrene and vinyl acetate, which are at opposite ends of the Q scale, are the individual k_{tr} values greater than their corresponding k_p values. Walling has observed a similar anomaly in transfer studies of

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[21] It is possible that the slow thermal decomposition of carbon tetrabromide contributed in part to the initiation step since the data in Table I indicate that the over-all rate of polymerization tends to increase with increasing ratios of [CBr_4]/[Monomer].

[22] C. C. Price, *J. Polymer Sci.*, **3**, 772 (1948).

[23] M. S. Matheson, E. E. Auer, E. B. Bevilacqua and E. J. Hart, THIS JOURNAL, **73**, 5395 (1951).

[24] Since k_p for methacrylonitrile has been determined at 30° only, the calculation of k_{tr} has been made from the value of C extrapolated to 30° from measurements at higher temperatures. Assuming a normal E_p value for this monomer, the magnitude of k_p calculated at 60° is considerably lower than that of styrene and it would appear that the order of increasing rate constants for propagation at 60° shown in Table III remains unchanged.

[25] (a) J. H. Baxendale and M. G. Evans, *Trans. Faraday Soc.*, **43**, 210 (1947); (b) M. G. Evans, *Faraday Society Disc.*, **2**, 271 (1947).

several of these monomers with *n*-butyl mercaptan and explained the results on the basis of the presence of additional ionic forms in the transition state arising from the transfer of an electron from the attacking radical to the transfer reagent, or *vice versa*.[6,11]

In the present case, if an electron is accepted by the attacking radical, R·, non-bonded resonance structures such as

$$\begin{array}{ccc} \overset{-}{\mathrm{R}}\overset{\cdot}{\mathrm{Br}}\overset{+}{\mathrm{C}}\mathrm{Br_3} & \overset{-}{\mathrm{R}}\overset{+}{\mathrm{Br}}\overset{\cdot}{\mathrm{C}}\mathrm{Br_3} & \overset{-}{\mathrm{R}}\overset{\cdot}{\mathrm{Br}}\mathrm{CBr_2}{=}\overset{+}{\mathrm{Br}} \\ \mathrm{I} & \mathrm{II} & \mathrm{III} \end{array}$$

may be drawn; or the following structures

$$\begin{array}{ccc} \overset{+}{\mathrm{R}}\overset{\cdot}{\mathrm{Br}}\overset{-}{\mathrm{C}}\mathrm{Br_3} & \overset{+}{\mathrm{R}}\overset{-}{\mathrm{Br}}\overset{\cdot}{\mathrm{C}}\mathrm{Br_3} & \overset{+}{\mathrm{R}}\overset{\cdot}{\mathrm{Br}}\mathrm{CBr_2}{=}\overset{-}{\mathrm{Br}}\ ^{26} \\ \mathrm{IV} & \mathrm{V} & \mathrm{VI} \end{array}$$

if an electron is donated by the attacking radical.

The increased transfer reactivity of styrene and vinyl acetate radicals, which are electron donors having $-e$ values,[10] contrasted with methyl acrylate, methyl methacrylate and methacrylonitrile which are electron acceptors having $+e$ values, indicates that only ionic forms such as IV–VI could contribute to the stability of the transition state.

In considering the relative reactivity of monomers in copolymerization reactions, Alfrey and Price[10,27] have proposed a semi-empirical relation known as the Q, e scheme. In terms of their parameters, a relationship analogous to that for relative reactivities in copolymerization may be expressed for transfer constants as

$$C = k_{tr}/k_{11} = Q_{tr}/Q_1 \exp\left[-e_1(e_{tr} - e_1)\right] \quad (10)$$

where Q_{tr} and Q_1 refer to the general reactivity of transfer agent and monomer, respectively, and e_{tr} and e_1 refer to their polarities. Using the transfer data of two monomers, whose Q and e values have been determined by copolymerization studies, equation 10 may be employed to calculate Q_{tr} and e_{tr} for any transfer reagent. When this calculation is performed with transfer data obtained from styrene and methyl methacrylate at 60°, the Q_{tr} and e_{tr} values obtained for carbon tetrabromide are 0.31 and +1.63, respectively. Table IV lists the values of Q_{tr} and e_{tr} for carbon tetrabromide obtained with all possible combinations of the presently studied monomers, exclusive of vinyl acetate. With the exception of the *p*-chlorostyrene–styrene combination, the agreement in Q_{tr} and e_{tr} values is consistent and fairly close. The transfer constants at 60° and the Q and e values of each monomer employed in the calculations of Q_{tr} and e_{tr} are listed in Table V, columns 2–4. Since several values are reported in the literature[22] for Q and e of methacrylonitrile and *p*-chlorostyrene, the actual values employed were the so-called "best" values recalculated by Alfrey, *et al.*,[28] in the case of *p*-chlorostyrene, and the values which gave the best fit to our data in the case of methacrylonitrile. In the latter case, the values employed are more in line with the observation that the general monomer reactivity is inversely related to the propagation rate constants (Table III) than the recalculated "best" values[28] wherein the Q of methacrylonitrile is less than that of styrene.

TABLE IV

CALCULATED VALUES OF Q_{tr} AND e_{tr} FOR CARBON TETRABROMIDE AT 60°

Monomer pair	Q_{tr}	e_{tr}
Styrene–methyl methacrylate	0.31	+1.63
Styrene–methyl acrylate	.32	1.62
Styrene–methacrylonitrile	.24	1.96
Styrene–*p*-chlorostyrene	.06	3.81
Methyl methacrylate–methyl acrylate	.30	1.54
Methyl methacrylate–methacrylonitrile	.43	2.40
Methyl methacrylate–*p*-chlorostyrene	.36	1.94
Methyl acrylate–methacrylonitrile	.58	2.64
Methyl acrylate–*p*-chlorostyrene	.37	1.89
Methacrylonitrile–*p*-chlorostyrene	.30	2.12

TABLE V

COMPARISON OF OBSERVED AND CALCULATED TRANSFER CONSTANTS AT 60°

Monomer	Q	e	$C_{obsd.}$	$C_{calcd.}$
Methacrylonitrile	1.5	+1.3	0.07[a]	0.14
p-Chlorostyrene	1.3	−1.0	5.2	3.1
Styrene	1.0	−0.8	2.2	(2.2)[b]
Methyl methacrylate	0.74	+ .4	0.27	(0.27)[b]
Methyl acrylate	.42	+ .6	0.41	0.40
Vinyl acetate	.01[c]	− .5[c]	>39	89

[a] Extrapolated from data at higher temperatures using the Arrhenius expression. [b] These values agree exactly with the observed transfer constants since the latter were used to establish e_{tr} and Q_{tr} appearing in equation 10. [c] Values chosen from copolymerization studies with vinyl chloride.

Using the Q_{tr} and e_{tr} values for carbon tetrabromide established from transfer measurements with styrene and methyl methylacrylate, transfer constants have been calculated for the other monomers. A comparison of the calculated and observed transfer constants is presented in Table V. It is noted that the calculated transfer constants predict the correct order of transfer reactivity of the monomers and in each case agree fairly closely with the experimental values.

The magnitude of the Q_{tr} and e_{tr} values calculated for carbon tetrabromide are noteworthy. Considering this reagent on the same basis as a vinyl monomer, it is apparent that the general reactivity of carbon tetrabromide is only slightly less than that of methyl acrylate. On the other hand, the high $+e$ value denotes that carbon tetrabromide serves as a strong electron acceptor and should exhibit a heightened reactivity with electron donor radicals. It is reasonable to expect that other transfer reagents exist having more negative e values than carbon tetrabromide and consequently exhibit a heightened reactivity with electron acceptor radicals. Indications that this situation may occur can be noted from chain transfer studies of styrene[3b] and methyl methacrylate[7] with carbon tetrachloride and isopropylbenzene. With the halogenated transfer reagent, styrene exhibits a higher transfer constant at 80° than methyl methacrylate, while the opposite order is found with the hydrocarbon transfer reagent.

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(26) In presenting this form it is assumed that bromine can expand its valence shell as has been suggested by R. M. Keefer and L. J. Andrews, THIS JOURNAL, **72**, 4677 (1950); **73**, 462 (1951).

(27) T. Alfrey and C. C. Price, *J. Polymer Sci.*, **2**, 101 (1947).

(28) Reference 10, pp. 92–103.

A comparison of the transfer constants of styrene and *p*-chlorostyrene (Table V) illustrates the sensitivity of the transfer constants toward small changes in the polarity of the monomer. Alfrey, *et al.*,[10] bring attention to the fact that the *Q*, *e* scheme is not very useful in analyzing small changes in reactivity such as would be caused by the introduction of a halogen atom into the ring of styrene. They determined as the "best" values of *Q* and *e* for *p*-chlorostyrene, $Q = 1.3$, $e = -1$; however, the shift from the values for styrene ($Q = 1$, $e = -0.8$) is of the same order of magnitude as the experimental uncertainties in *Q* and *e*. The question is raised, therefore, as to whether or not the substitution of a chlorine atom in the *para* position of styrene actually confers a more electron donating character to the monomer. Our studies reveal an appreciably greater transfer constant for *p*-chlorostyrene than styrene and thereby indicate a higher electron donating character for the *p*-chlorostyryl radical. The higher transfer constant for *p*-chlorostyrene is not associated with the change in monomer reactivity (the *Q* term) since this factor should tend to lower the transfer constant for the more resonance stabilized *p*-chlorostyryl radical.

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Heat of Adsorption of Argon Adsorbed on Titanium Dioxide between 60 and 90°K.

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The heat of adsorption of argon on titanium dioxide has been measured with a modified Nernst–Giauque calorimeter at temperatures of 63.5, 73.0, 78.5 and 86.5°K. for concentrations ranging to a maximum value of the order of a monolayer. The heat capacity of the adsorbed phase was determined between 55 and 90°K. in the same range of concentrations. By using the heat capacity data it was found possible to reduce the experimentally determined differential heats of adsorption at 73.0, 78.5 and 86.5 to a single curve at 63.5°K. within the experimental error. Therefore, at these temperatures, it is believed that the experimental method has yielded thermodynamically reversible results. The results of the experimental measurements at 63.5°K. do not fall on the single curve, and consequently the adsorption process appears to be metastable at this temperature. The differential heat curves for the equilibrium and non-equilibrium processes have been used to determine the corresponding energy distribution at the sites of adsorption.

Introduction

The present work is concerned with a calorimetric investigation of the heat of adsorption of argon adsorbed on a sample of titanium dioxide between 60 and 90°K. The concentrations of the adsorbed argon were dilute, the maximum value being approximately the monolayer capacity. The results of such measurements are of interest because of the knowledge they provide on the distribution of energy among the adsorbent sites.

The heat of adsorption and the heat capacity of argon adsorbed on another sample of titanium dioxide has been measured calorimetrically by Morrison and co-workers[1,2] in the 85 to 140°K. range. Coverages in both the monolayer and multilayer region were used. Good agreement was obtained between the heat capacity as measured directly or as derived from the temperature coefficient of the integral heats of adsorption. Consequently, there is good reason to believe that the properties measured in this case were the reversible thermodynamic properties of the system.

No measurements of the heats of adsorption below 85°K. were made by the group above, because thermal equilibrium at the lowest coverages was reached only after a period of several hours. We have also noted this slow approach to equilibrium for low coverages at temperatures around 70°K. but at temperatures above and below this value, an *apparent* equilibrium is attained rapidly even at low concentrations of adsorbed argon. This is of interest because of the bearing it may have on two studies which have utilized argon adsorbed on graphite, the results of which appear contradictory at this time. Jura and Criddle[3] have reported stepwise isotherms for argon adsorbed on graphite between 60 and 65°K. On the other hand, Crowell and Young[4] have observed only smooth isotherms at low coverages of argon adsorbed on graphite from 80 to 90°K. Even though the present work employs a different surface, our results, which overlap the range of temperatures used in the preceding two studies, may help provide an explanation for the phenomena which have been observed.

Experimental

The calorimeter is a modification of the Nernst–Giauque type.[5,6] A schematic drawing of the apparatus is shown in Fig. 1.

The calorimeter vessel of about 100-ml. capacity was filled with 60 g. of finely divided titanium dioxide in the rutile form. The sample of rutile was designated as No. MP 578-3 by the National Lead Company. It was 94.3% titanium dioxide with the remainder being water, adsorbed or coördinately bound. The sample was activated under a high vacuum at 180° for 72 hours until the pressure dropped below 10^{-6} mm. The monolayer capacity of the sample as determined by the BET method[7] at 77.6°K. was 0.0541 mole using argon as the adsorbate.

Temperatures and temperature differences during the measurements were determined by a four-lead, strain-free platinum resistance thermometer. The resistance thermometer was calibrated between 55 and 90°K. against a copper–constantan thermocouple which previously had been

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[1] J. A. Morrison, J. M. Los and L. E. Drain, *Trans. Faraday Soc.*, **47**, 1023 (1951).

[2] L. E. Drain and J. A. Morrison, *ibid.*, **48**, 840 (1952).

[3] G. Jura and D. Criddle, *J. Phys. Colloid Chem.*, **55**, 163 (1951).

[4] A. D. Crowell and D. M. Young, *Trans. Faraday Soc.*, **49**, 1080 (1953).

[5] H. Nernst, *Ann. Physik.*, **36**, 1395 (1911).

[6] W. F. Giauque and C. J. Egan, *J. Chem. Phys.*, **5**, 45 (1937).

[7] S. Brunauer, P. H. Emmett and E. Teller, THIS JOURNAL, **60**, 309 (1938).