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

The Mechanism of Bromine Addition to 1,3-Butadiene[1]

BY LEWIS F. HATCH, PETE D. GARDNER AND RONALD E. GILBERT

RECEIVED FEBRUARY 28, 1959

The effect of solvent on the bromination of butadiene has been reinvestigated. Contrary to a previous report, the ratio of 1,2- to 1,4-bromination is not solvent dependent. The existence of a cyclic intermediate (or transition state) is suggested. Unimolecular kinetics of the rearrangement of 3,4-dibromo-1-butene to *trans*-1,4-dibromo-2-butene and a large negative entropy of activation are consistent with this mechanism. The abnormal reduction of 3,4-dibromo-1-butene to *trans*-2-butene is also described and the probable mechanism of this reaction is discussed.

It is well established that the products of the addition of bromine to 1,3-butadiene are 3,4-dibromo-1-butene (I), *trans*-1,4-dibromo-2-butene (II) and two stereomeric tetrabromobutanes.[2-4] Proper selection of experimental conditions makes it possible to prepare a mixture of the dibromides essentially free of tetrabromides.[2] The ratio of the two dibromides was reported by Farmer, Lawerence and Thorpe[2] to be dependent upon the nature of the solvent used for the reaction, the composition varying from 38.4% of II in hexane to 70.0% of II in acetic acid. Thus, it would appear that the formation of I and II is kinetically controlled with II being favored by more polar solvents. Unfortunately these data, and therefore any conclusions which might be drawn from them, are clouded by the fact that I and II both undergo rearrangement to an equilibrium mixture of the two. While this is a slow rearrangement at low temperatures, it occurs sufficiently rapidly to preclude accurate analysis of mixtures of I and II by conventional isolation techniques.

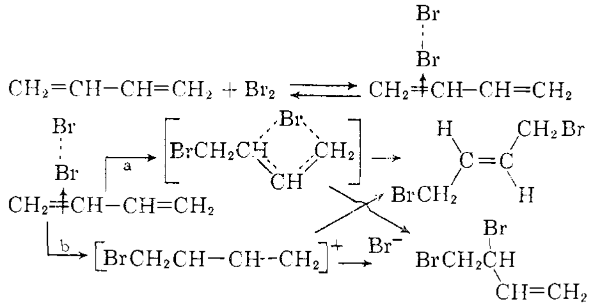
Since the presence or absence of a solvent effect bears strongly on the question of the reaction mechanism, the work has now been repeated with greater precision and accuracy in the preparation and analysis of the reaction mixtures. Analyses were made using infrared spectra of appropriately diluted reaction mixtures. The quantitative data confirm that I and II are the products of the reaction with only small amounts of tetrabromobutanes and no *cis*-1,4-dibromo-2-butene being formed. Data related to the influence of solvent are given in Table I.

TABLE I

EQUIMOLAR BROMINATION OF 1,3-BUTADIENE IN VARIOUS SOLVENTS AT −15°

Solvent	1,4-Dibromo-2-butene (1,4-addition), %
Carbon disulfide	48
Trichloroethylene	49
Chloroform	45
Carbon tetrachloride	50
Hexane	46

These data indicate that, within the limits of experimental error, there is no dependence of the ratio I/II on solvent polarity.[5] The two most reasonable mechanisms for the reaction are[6,8]:



The transition state depicted in route b should require more extensive solvation than that involved in route a. Of these two possibilities then, (a) would seem the more likely. It is not possible to *predict* the extent to which the attainment and further reaction of this transition state are dependent upon solvent polarity but it is quite reasonable to assume it to be less than in the case of the route b transition state. This cyclic intermediate which was originally suggested by Farmer, Lawerence and Thorpe,[2] although not consistent with their data, appears to have some experimental justification.

A further requirement placed on a mechanistic interpretation is an explanation of the complete stereospecificity of the reaction (all of the 1,4-isomer is *trans*). An inspection of molecular models of the two possible configurations of this transition state[9] indicates that the form intermediate to the *trans* configuration of II is more likely from the standpoint of the conformation of the butadiene

---

(1) Presented before the Symposium of "Solvent Effects in Organic Reaction Mechanism," London Chemical Society, Queen Mary College, London, July, 1957.

(2) E. H. Farmer, C. D. Lawerence and J. F. Thorpe, *J. Chem. Soc.*, 729 (1928).

(3) K. Mislow, THIS JOURNAL, **75**, 2512 (1953).

(4) Ya. M. Slobodin and S. A. Zaboev, *Zhur. Obshchei Khim.* (*J. Gen. Chem.*), **22**, 603 (1952); *C. A.*, **46**, 7433 (1952). However, see also Ya. M. Slobodin, *ibid.*, **24**, 444 (1954); *C. A.*, **49**, 6080 (1955).

(5) Acetic acid was not studied as a solvent as its m.p. necessitated use of a higher temperature during bromination. Data from such a run would be of questionable value for comparison with the results obtained from other solvents.

(6) Another mechanism involving "frontal" attack by the bromine molecule was rejected for the same arguments invoked by Mislow and Hellman[7] for the chlorination reaction.

(7) K. Mislow and H. M. Hellman, THIS JOURNAL, **73**, 244 (1951).

(8) For general discussion concerning placement of the attacking bromine atom at the terminal position, see G. W. Wheland, "Resonance in Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1955, p. 459.

(9) It should be noted that two forms of this transition state are possible, one having the four carbon atoms planar in the *s-trans* conformation and the other in the *s-cis*. In either of these, the formally non-bonded bromine atom lies in the molecular orbital of the three sp^2 carbon atoms. The *s-trans* form, that required by the observed *trans* geometry in the product, would result from an initial attack of bromine on the *s-trans* form of butadiene. This seems very likely to be the case. If, on the other hand, it were theoretically possible for the *s-cis* attack to result in an *s-trans* transition state (by some obscure re-hybridization), it would probably occur as a result of steric factors; the *s-trans* form is the more sterically favored of the two.

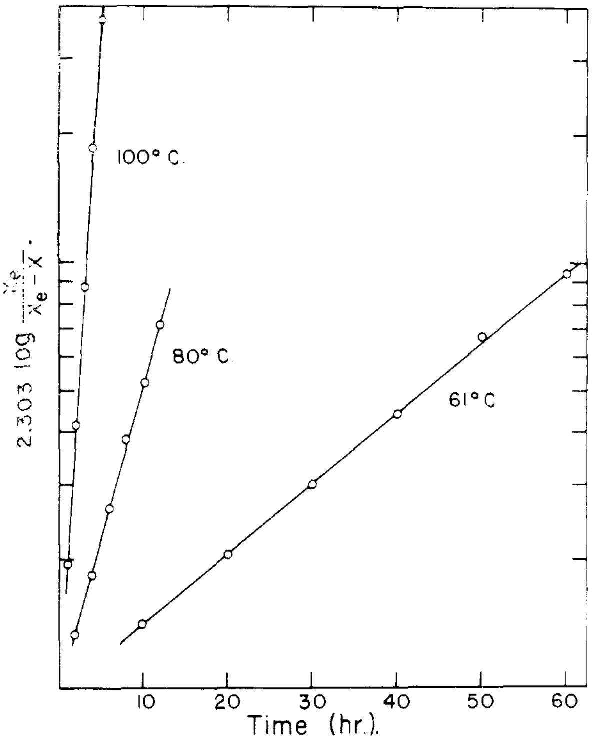


Fig. 1.—Rates of isomerization of 3,4-dibromo-1-butene to *trans*-1,4-dibromo-2-butene.

molecule as well as from steric considerations.[9] The chlorination of butadiene is also reported to give only the *trans* 1,4-isomer.[7]

It is of interest to note that theoretically-based predictions on the 1,4-/1,2-halogenation ratio favor the 1,4-isomer.[10,11]

The rearrangement of I to II was studied kinetically to corroborate the proposed mechanism. While the formation of I and II by bromine addition to 1,3-butadiene is unquestionably kinetically controlled, the transition state involved in their interconversion is probably identical with that considered for the addition reaction. Thermodynamic data for this isomerization are in Table II; rate data are in Table III.

TABLE II

THERMODYNAMIC FUNCTIONS FOR THE ISOMERIZATION OF 3,4-DIBROMO-1-BUTENE TO *trans*-1,4-DIBROMO-2-BUTENE

Function	Temperature, °K. 334	353	373
trans-1,4-Dibromo-2-butene (II), %	90.5	88.0	85.5
K_{eq}, l. mole^{-1}	9.53	7.33	5.86
ΔF, kcal. mole^{-1}	−1.49	−1.40	−1.31
ΔS, e.u.	−4.84	−4.51	−4.19
ΔH, kcal. mole^{-1}	−3.10	−2.99	−2.87

The reaction was unimolecular. Although the equilibrium could be established from either side, kinetic data were obtained only from I. Specific rate constants, defined as $k = X_e/at \ln (X_e/X_e - X)$, were determined from a plot of $\ln X_e/X_e - X$ *vs.* time (Fig. 1) where X is mole-concentration of I at time t, a is initial mole-concentration of I and X_e is the mole-concentration of I at equilibrium. Equilibrium constants, defined as $K_{eq} = [II]/[I]$ and equal to k_1/k_{-1} at a given temperature, were also required for these calculations.[12]

TABLE III

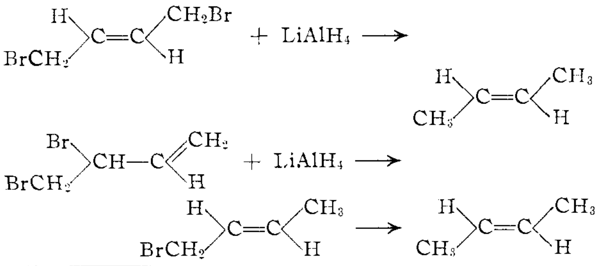
RATE CONSTANTS FOR THE ISOMERIZATION OF 3,4-DIBROMO-1-BUTENE TO 1,4-DIBROMO-2-BUTENE

T, °K.	Slope of $\ln X_e/X_e\text{-}X$ *vs.* t	k_1, hr.$^{-1}$	k_{-1}, hr.$^{-1}$
334	0.0380	0.034	0.004
353	.167	.147	.020
373	.745	.635	.110

A plot of $\ln K_{eq}$ against $1/T$ gives a straight line.

Rate data permitted calculations of the frequency factor, $A = 5.1 \times 10^{10}$ sec^{-1}, activation energy, $E_a = 18.6$ kcal./mole, and entropy of activation, $\Delta S^{\ddagger} = -12.6$ e.u. The solvent used in the isomerization study (n-decane) will not cause large changes in the solvation sphere as I goes into the transition state and it is quite reasonable, therefore, to attribute the low $\Delta S^{\ddagger}$ value to a minor change in molecular geometry as the transition state develops. It has been established that cyclic transition states give rise to rather large negative activation entropies and low frequency factors.[13]

Early in the course of this study, a method of product analysis was planned which was based on the reductive dehalogenation of a reaction mixture by lithium aluminum hydride. The final analysis of the resulting hydrocarbon mixture would have been by gas chromatography. It is known that primary allylic halides may be reduced by lithium aluminum hydride without double bond migration[14,15] and without alteration of double bond geometry.[15] Abnormal reduction has been reported,[16] however, and it was necessary to determine whether or not this was typical of the behavior of all secondary allylic halides. The reaction of lithium aluminum hydride with *trans*-1,4-dibromo-2-butene, 3,4-dibromo-1-butene (92.5%), a mixture of the two and the reaction product from the addition of bromine to 1,3-butadiene in chloroform at −15° gave *only* *trans*-2-butene as indicated by gas chromatography (Fig. 2). The 1,4-isomer underwent reduction in the reported manner,[14] but the 3,4-isomer isomerized stereospecifically during the course of the reaction.



---

[10] G. B. Heisig, THIS JOURNAL, **55**, 1297 (1933).

[11] F. L. Pilar, *J. Chem. Phys.*, **29**, 1119 (1958).

[12] K. J. Laidler, "Chemical Kinetics," McGraw-Hill Book Co., Inc., New York, N. Y., 1950, pp. 19–20.

[13] *Cf.* A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," John Wiley and Sons, Inc., New York, N. Y., 1953, p. 106.

[14] L. W. Trevoy and W. G. Brown, THIS JOURNAL, **71**, 1675 (1949).

[15] L. F. Hatch and R. H. Perry, *ibid.*, **71**, 3262 (1949).

[16] L. F. Hatch and J. J. D'Amico, *ibid.*, **73**, 4393 (1951).

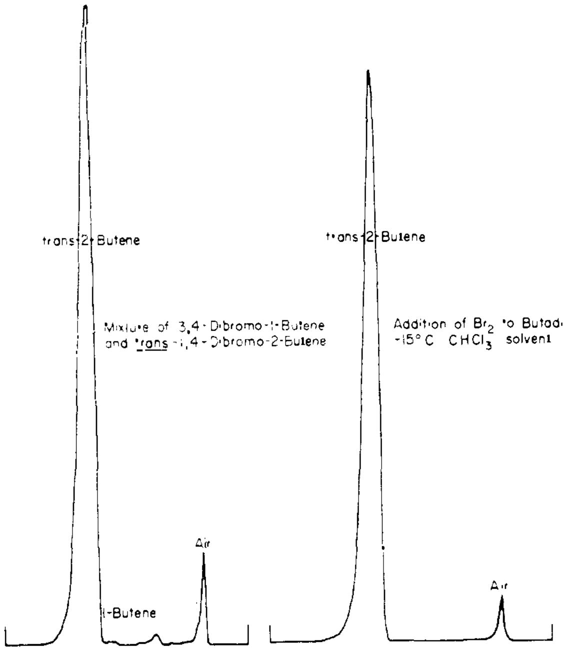
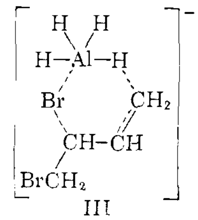


Fig. 2.—Gas chromatographic analysis of the lithium aluminum hydride reduction of a mixture of 3,4-dibromo-1-butene and 1,4-dibromo-2-butene and of the addition products from the addition of bromine to butadiene in chloroform at −15%.

It is possible that I undergoes initial rearrangement to II which is then reduced normally. This is not probable, however, because of the speed of reduction (qualitative observation) relative to that of isomerization. A more plausible interpretation is that shown in the preceding reaction sequence. The combination of the relatively large size of the AlH_4^- ion and the inaccessability of the carbon atom to which the secondary bromine atom is attached would make a normal SN2 attack by AlH_4^- very difficult. Attack at the terminal carbon atom (abnormal or SN2′ reaction), on the other hand, would not only be free of steric effects but should be facilitated by attraction between the aluminum atom and the leaving bromide ion (III). This



III

has been suggested as an important feature of some SN2′ reactions[17] and is consistent with its stereochemistry.[18] The complete stereospecificity of the reduction is still unexplained, however, as no particular double bond geometry in the product has been previously recorded for the SN2′ reaction. It is clear from the work of Young and Wilk[19] that both isomers may be formed. An inspection of molecular models reveals that there is considerably less steric interaction in that form of III expected to give *trans*-2-butene than in the other form. It is assumed in these considerations that the two bromine atoms are disposed *trans* to each other and that the interaction of the π-electron cloud of the double bond and a bromine atom constitutes a steric repulsion. The previously reported stereospecific abnormal reduction[16] of 2,3,3-trichloro-1-butene to *trans*-2,3-dichloro-2-butene is also the result of halogen repulsion. The conformation necessary for the *cis* product would force three chlorine atoms into direct opposition. It seems doubtful that the observed stereospecificity in these two instances will prove to be general of SN2′ reductions by lithium aluminum hydride. It appears likely, however, that all secondary allylic halides will be reduced by this reagent, at least partially, in the abnormal manner.

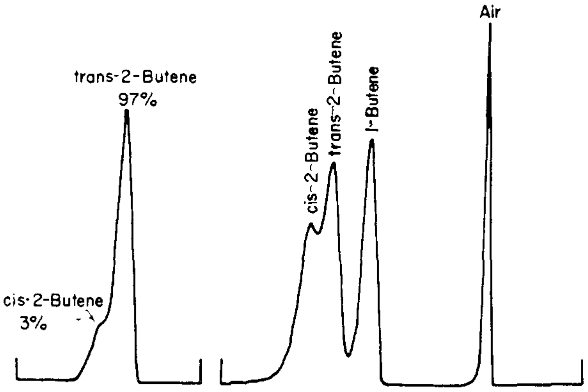


Fig. 3.—Gas chromatographic analysis of a mixture of 1-butene, *cis*- and *trans*-2-butene and of a mixture containing 97% *trans*- and 3% *cis*-2-butene.

Experimental

Bromination of 1,3-Butadiene.—To a cold solution (−15°) of 54.0 g. of 1,3-butadiene in 150 ml. of *n*-hexane was added 160 g. of bromine dropwise and with vigorous stirring. After completion of the addition, the temperature of the mixture was lowered to −30° and the solid *trans*-1,4-dibromo-2-butene (II) removed by suction filtration. Recrystallization from *n*-hexane afforded pure II, m.p. 54°. Fractional distillation of the filtrate through a 1 × 36 in. helices-packed column gave 3,4-dibromo-1-butene (I), b.p. 21° (1.5 mm.), $n^{20}\mathrm{D}$ 1.541, $n^{25}\mathrm{D}$ 1.538, $n^{30}\mathrm{D}$ 1.535, d_{20} 1.839, d_{25} 1.830, d_{30} 1.816. Its purity (infrared) was 92.5%. This substance isomerized slowly at 25° to II.

Infrared spectrograms of known concentrations of I and II in various solvents were determined. Each compound showed characteristic absorption bands suitable for quantitative analysis and these obeyed Beer's law over the entire concentration range used. As a consequence of this, it was possible to extrapolate to true extinction coefficients of 100% pure material at each of the wave lengths used in the analysis. Wave length values were 8.80 and 10.75 μ for I and 8.30 and 10.40 μ for II. No absorption was observed in any spectrogram which could not be assigned to I or II. Percentage of I and II totaled *ca.* 99 indicating that less than 1% of tetrabromides were formed under the bromination conditions used.

Study of Solvent Effect.—The following is the bromination procedure used in all solvent runs. Change of solvent was the only variable. To a solution of 6.5 g. of butadiene in 90 ml. of solvent (see Table I), which had been cooled to −15° and maintained at that temperature, was added 19.2 g. of bromine dropwise and with vigorous stirring. Upon completion of the addition, the reaction mixture was diluted to exactly 100 ml. with more solvent. Percentage transmissions at the indicated wave lengths were read on a Baird double-

---

[17] W. G. Young, I. D. Webb and H. L. Goering, THIS JOURNAL, **73**, 1076 (1951).

[18] G. Stork and W. N. White, *ibid.*, **75**, 4120 (1953).

[19] W. G. Young and I. J. Wilk, *ibid.*, **79**, 4793 (1957).

beam instrument using an identical solvent-filled cell in the reference beam. The percentage of I and II in each mixture was then calculated from extinction coefficients previously determined at each wave length. These data are summarized in Table I.

Isomerization Study.—The isomerization of I to II was carried out at 61.2, 80.1 and 100.0° by thermostating solutions of known concentration of I in *n*-decane. Samples were removed for analysis (done as described previously) at times which gave a good conversion–time curve at each temperature. A plot of ln $X_e/(X_e-X)$ *vs.* time for each temperature is shown in Fig. 1. Thermodynamic values and rate data are summarized in Tables II and III, respectively.

Lithium Aluminum Hydride Reduction.—Bromine was added to butadiene in chloroform at −15° in the manner previously described. After addition of the bromine was complete the chloroform was flashed off under reduced pressure at the reaction temperature and tetrahydrofuran was added to replace the chloroform. Lithium aluminum hydride in tetrahydrofuran was added at −18 to −15° and a temperature of −15° was maintained for two hours. The reaction mixture was then heated to reflux temperature (67°) and held at that temperature for three hours. The reaction products were distilled into a cold trap (Dry Ice-acetone), weighed and analyzed by gas chromatography (Fig. 2). Only one product was formed, *trans*-2-butene, and the material balance on the butadiene was 99%.

Figure 2 also contains data obtained from the lithium aluminum hydride reduction of a mixture of 3,4-dibromo-1-butene and 1,4-dibromo-2-butene. Similar treatment of 92.5% 3,4-dibromo-1-butene and pure 1,4-dibromo-2-butene gave *trans*-2-butene as the only product with a yield of 95% or higher. Analysis of a mixture of the three olefins possible (1-butene, *cis*- and *trans*-2-butene) and of a 97% *trans*- 3% *cis*-2-butene mixture are given in Fig. 3.

The gas chromatographic equipment used for analysis consisted of a 10 ft. × 1/4 in. copper column with dinonyl phthalate on fire brick as the packing. The detector unit was a Gow-Mac thermal conductivity cell and helium was the carrier gas.

Acknowledgment.—The authors are indebted to The Robert A. Welch Foundation for the financial support of this research and to W. H. R. Shaw for valuable discussions concerning the kinetic studies.

AUSTIN 12, TEX.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF FLORIDA]

The Formation of Linear Polymers from Diene Monomers by a Cyclic Polymerization Mechanism. III. A Study of the Structure of Cyclic Polymers of Certain Unsymmetrical 1,6- and 1,7-Dienes[1,2]

BY MARTIN D. BARNETT,[3a] ALLAN CRAWSHAW[3b] AND GEORGE B. BUTLER

RECEIVED APRIL 25, 1959

The methyl allyl, methyl 2-butenyl and methyl 3-butenyl mixed esters of maleic and fumaric acid have been synthesized and polymerized in bulk using benzoyl peroxide to afford a series of low molecular weight linear polymers containing 37–77% residual unsaturation. The properties of the polymers indicated that polymerization had occurred by an intramolecular-intermolecular mechanism leading, in part, to a poly-[3(5)-methylene-4-carbomethoxy-δ-valerolactone] or (in the case of the 3-butenyl esters) to a poly-[3(5)-methylene-4-carbomethoxy-ε-caprolactone] structure. In addition, poly-(methyl allyl maleate) and poly-(methyl 2-butenyl maleate) showed absorption at 1780 cm.$^{-1}$ characteristic of a γ-butyrolactone ring system. This band was lacking in the corresponding fumarates. Possible explanations of the various modes and relative degrees of cyclization in the polymers are presented.

Recent work[4-10] has verified the original proposal[11] that certain monomers containing a 1,6-diene system can, on polymerization, undergo an alternating intramolecular–intermolecular chain propagation or cyclization, leading to the formation of saturated linear chains containing alternating six-membered rings and methylene groups. In addition, extensions of this new chain propagation mechanism to diene systems capable of forming rings containing more than six carbon atoms[12] as well as into the copolymer field[13] have now been reported.

Work in this area thus far has been largely limited to the study of symmetrical 1,6-dienes. Unsymmetrical 1,6-dienes, however, also should be capable of homopolymerization *via* cyclization, especially those monomers containing double bonds of comparable reactivity toward copolymerization. Although the homopolymerizations of such unsymmetrical 1,6-dienes as allyl acrylate,[14] allyl methacrylate[15,16] and substituted allyl methacrylates[17] have been reported, there appears to have been no previous study directed specifically toward verification of the presence of cyclic units in the polymer derived from such dienes. Unsaturated esters of maleic and fumaric acid seemed particularly suited for such a study because systems of this type should permit a qualitative comparison of the relative reactivities of various unsaturated alcohols as well as a comparison of the degree of cyclization in the *cis–trans* isomers.

---

(1) This research was supported by the United States Air Force through the Air Force Office of Scientific Research of the Air Research and Development Command, under Contract Number AF18(603)-116. Reproduction in whole or in part is permitted for any purpose of the United States government.

(2) This paper was presented before the Division of Polymer Chemistry, American Chemical Society, Boston, Mass., April, 1959.

(3) (a) Post-doctoral fellow, 1958–1959; (b) Post-doctoral fellow, 1956–1958.

(4) G. B. Butler, A. Crawshaw and W. L. Miller, THIS JOURNAL, **80**, 3615 (1958).

(5) A. Crawshaw and G. B. Butler, *ibid.*, **80**, 5464 (1958).

(6) C. S. Marvel and R. D. Vest, *ibid.*, **79**, 5771 (1957).

(7) C. S. Marvel and R. D. Vest, *ibid.*, **81**, 984 (1959).

(8) C. S. Marvel and J. K. Stille, *ibid.*, **80**, 1740 (1958).

(9) J. F. Jones, *J. Polymer Sci.*, **33**, 7 (1958).

(10) J. F. Jones, *ibid.*, **33**, 15 (1958).

(11) G. B. Butler and R. J. Angelo, THIS JOURNAL, **79**, 3128 (1957).

(12) (a) C. S. Marvel and W. E. Garrison, Jr., *ibid.*, **81**, 4737 (1959); (b) T. Holt and W. Simpson, *Proc. Roy. Soc.* (*London*), **A238**, 154 (1956); (c) M. Oiwa and Y. Ogata, *J. Chem. Soc. Japan*, **79**, 1506 (1958).

(13) W. H. Schuller, J. A. Price, S. T. Moore and W. M. Thomas, *J. Chem. Eng. Data*, **1**, in press (1959).

(14) L. Gindin, S. Medvedev and E. Flesher, *J. Gen. Chem.* (*U.S.S.R.*), **19**, a127 (1949).

(15) E. R. Blount and B. E. Ostberg, *J. Polymer Sci.*, **1**, 230 (1946).

(16) S. G. Cohen, B. E. Ostberg, D. B. Sparrow and E. R. Blount, *ibid.*, **3**, 264 (1948).

(17) G. M. Bristow, *Trans. Faraday Soc.*, **54**, 1064 (1958).