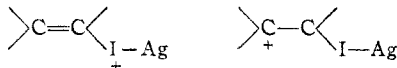


benzene-silver ion complex which is stabilized by resonance forms involving the benzene ring. A similar structure based on resonance forms of the type

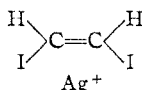


may be appropriate to describe the argentation of the vinyl bound iodine atom.

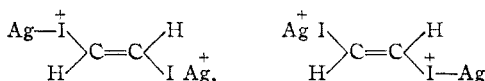
The equilibrium constants indicate that the tendency for monoargentation is considerably higher for the *cis* than for the *trans* isomer of 1,2-diiodoethylene. On the other hand the  $K_2$  value for the *cis* compound is approximately one-half that of the *trans*. This suggests that a steric effect opposing addition of a second silver ion is operative with *cis*  $\text{AgD}^+$  which is lacking for the corresponding complex ion of the *trans* isomer.<sup>13</sup>

It occurred to the authors that *o*-diiodobenzene,

(13) The fact that the  $K_1$  value for the *cis* diiodide is so much larger than that for the *trans* isomer suggests that in the *cis*  $\text{AgD}^+$  ion the silver may be located in a position such that it may bond to either of two iodine atoms. The geometry of such a structure is indicated by the formula



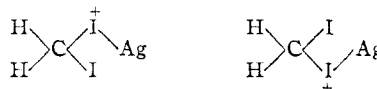
Professor George Scatchard has pointed out to the authors that from statistical considerations one would predict that these diiodides would have  $K_2$  values not more than one-fourth as large as their  $K_1$  values, provided only  $\text{Ag}^+$ -iodine atom complexes were formed. It is possible that the  $\text{Ag}_2\text{D}^{++}$  complex for the *trans* isomer derives some stabilization energy from the contribution of equivalent no bond resonance forms



A similar explanation may be presented in the cases of the *m*- and *p*-diiodobenzenes. A correct prediction as to the relative magnitudes of  $K_1$  and  $K_2$  is in this case difficult, since double bond or ring argentation must occur at least to a small extent with the diiodo-ethylenes and -benzenes.

in which the two iodine atoms are oriented with respect to each other in much the same manner as are the two iodine atoms in *cis*-1,2-diiodoethylene, might have a  $K_1$  value much larger than those for the *m*- and *p*-diiodides. Experiment confirmed this supposition. Values of  $K_1$  for the *o*-, *m*- and *p*-isomers were, respectively, 16.5, 5.7 and 5.5<sup>1</sup>. The  $K_2$  value for the *ortho* compound was lower than that for either the *m*- or *p*-derivative. Indeed the  $K_1$  and  $K_2$  values for *o*-diiodobenzene and for the *cis*-diiodoethylene were closely similar. It should be noted, however, that too close a comparison of these values is not justified since there is some doubt as to the purity of the "*cis*" diiodoethylene sample.<sup>6</sup>

It is interesting to note that while the  $K_1$  value for methylene iodide is of the same order of magnitude as those values for *cis*-diiodoethylene and for *o*-diiodobenzene, there seems to be no evidence of an appreciable reaction to form a 2:1 silver ion-methylene iodide complex. It is probable that the lack of evidence for this 2:1 complex may be ascribed to the very close proximity of the two iodine atoms in the saturated diiodide. The structure of the 1:1 methylene iodide complex actually may be stabilized sufficiently by resonance forms of the type



so as to inhibit strongly reaction to coordinate a second silver ion.

Experiments to determine the degree to which saturated alkyl monoiodides form argentation complexes would be most interesting in connection with some of the postulates as to the structure of the complexes. Unfortunately no iodide suitable for such a study has yet been discovered.

DAVIS, CALIFORNIA

RECEIVED JUNE 29, 1951

[CONTRIBUTION NO. 115 FROM THE GENERAL LABORATORIES OF THE UNITED STATES RUBBER COMPANY]

## Copolymerization. XVIII.<sup>1,2</sup> The Reactivity of Butadiene in Emulsion Copolymerization at 5°

BY CHEVES WALLING<sup>3</sup> AND JOHN A. DAVISON

The compositions of synthetic rubbers derived from butadiene have been studied. Monomer reactivity ratios have been determined for the copolymerization of butadiene with methyl methacrylate, methyl acrylate, butyl acrylate, methacrylonitrile and vinylidene chloride in emulsion at 5°. In the copolymerization of butadiene with acrylate esters there is a tendency toward alternation. Butadiene is shown to behave much like styrene in copolymerization. Styrene therefore serves as a substitute for butadiene in oil-phase polymerizations, where the polymerization of butadiene is inconveniently slow.

Despite the importance of butadiene as a component of synthetic rubbers, the composition of butadiene copolymers has received little quantitative study. Thus, the only systems for which monomer reactivity ratios are available are those containing, as the other monomer, styrene,<sup>4,5,6</sup>

*p*-chlorostyrene,<sup>7</sup> 2,5-dichlorostyrene,<sup>7</sup> 1-cyanobutadiene,<sup>7</sup> methyl methacrylate,<sup>4</sup> acrylonitrile<sup>6,7,8</sup> and 2-chlorobutadiene.<sup>8</sup> Accordingly, we have recently determined the monomer reactivity ratios in the copolymerization of butadiene with several rates in the copolymerization of butadiene with

(1) For the preceding paper in this series see C. Walling and E. A. McElhill, *THIS JOURNAL*, **72**, 2927 (1950).

(2) This work was carried on under Quartermaster Contract W44-109-QM-2030.

(3) Present address, Lever Brothers Co., Cambridge, Mass.

(4) F. M. Lewis, C. Walling, W. Cummings, E. R. Briggs and W. J. Wenisch, *THIS JOURNAL*, **70**, 1527 (1948).

(5) E. J. Meehan, *J. Polymer Science*, **1**, 318 (1946).

(6) J. M. Mitchell and H. L. Williams, *Can. J. Research*, **27F**, 35 (1949).

(7) F. T. Wall, R. W. Powers, G. D. Sands and G. S. Stent, *THIS JOURNAL*, **70**, 1031 (1948).

(8) L. M. Gindin, A. D. Abkin and S. S. Medvedev, *J. Phys. Chem. (U. S. S. R.)*, **21**, 1267 (1947).

several monomers, employing emulsion polymerization at 5°. Two factors suggested this choice. First, widespread technical interest in low-temperature emulsion polymerization made it desirable to determine monomer reactivity ratios under these conditions. Second, use of low temperatures and an emulsion technique (to give high polymerization rates) decreases the possibility of interference by a competing Diels-Alder reaction between butadiene and the dienophile monomers employed. Further, in view of the work of Fordyce, Chapin and Ham,<sup>9</sup> of Smith<sup>10</sup> and of Wall, Florin and Delbecq,<sup>11</sup> it is probable that the monomer reactivity ratios are essentially those which would be observed in the homogeneous reaction (if it could be carried out at the same temperature<sup>12</sup>) since all the monomers are preferentially soluble in the non-aqueous phase.

**Experimental polymerizations** were carried out in 750-ml. capped bottles rotated in a 5° thermostat, employing the essentially conventional recipe given in Table I.

TABLE I  
EMULSION POLYMERIZATION RECIPE

Total monomers, g.	100.0
MTM-4, <sup>b</sup> g.	0.10-0.20
Cumene hydroperoxide, g.	0.08-0.15
FeSO <sub>4</sub> ·7H <sub>2</sub> O, g.	0.15-0.30
K <sub>4</sub> P <sub>2</sub> O <sub>7</sub> , g.	0.18-0.36
Dresinate 214, <sup>c</sup> g.	5.0
Water	180.0

<sup>a</sup> Commercial materials. <sup>b</sup> A mixed tertiary mercaptan manufactured by the Phillips Petroleum Company. <sup>c</sup> Potassium salt of a disproportionated rosin acid supplied by the Hercules Powder Company.

The quantity of mercaptan was adjusted to give a product of convenient degree of polymerization. The quantities of oxidation-reduction components were selected to give an Fe<sup>++</sup>/K<sub>4</sub>P<sub>2</sub>O<sub>7</sub> molar ratio of unity and the polymerization rate adjusted by varying the peroxide/Fe<sup>++</sup> ratio from 0.8 to 3.0. Bottles were loaded in the conventional manner, water, soap, iron and pyrophosphate being added first, the bottles cooled, charged with monomer and mercaptan, capped, and the peroxide injected with a hypodermic needle through a self-sealing rubber gasket in the bottle cap.

**Polymer Treatment.**—Yields were obtained by determining the total amount of solids remaining from a weighed sample of latex (approximately 2 g.) after drying 10 minutes at 100–120° and correcting for a weight of the non-volatile components of the polymerization recipe and the evaporation of butadiene before the initial weighing. The technique is essentially the standard one in the synthetic rubber industry.<sup>13</sup> Polymer was isolated for analysis by coagulation of a portion of the

latex with methanol, several alternate benzene solutions and methanol precipitations of the separated polymer to remove soap and unreacted monomers, and final isolation by dissolving in benzene, freezing, and removing the solvent by vacuum sublimation. Isolated polymers were, in general, stored in a refrigerator in the dark to minimize oxidation before analysis.

**Treatment of Data.**—Experimental results on the five systems studied are presented in Table I. Monomer reactivity ratios were determined in the usual way by graphical solution of the copolymerization equation,<sup>14,15</sup> but plots of the data have been omitted in the interest of brevity. Since experiments were carried out at three initial feeds for each system, monomer reactivity ratios have been taken as the center of gravity of the separate intersections. Experimental errors have been estimated as the standard deviations of results from separate intersections, or as the uncertainty arising from analytical error (0.2%), whichever is the larger, according to previous practice.<sup>16</sup> The only deviation from this technique is for the butadiene-vinylidene chloride system, for which the actual intersection is negative ( $r_1 = -0.03$ ) so that  $r_1$  has been estimated arbitrarily as <0.05.

TABLE II  
EMULSION COPOLYMERIZATIONS OF BUTADIENE M<sub>1</sub> AT 5°

[M <sub>1</sub> ] <sup>a</sup>	[M <sub>2</sub> ] <sup>a</sup>	$\frac{[M_1]_0}{[M_1]_0 - [M_1]}$	$\frac{[M_2]_0}{[M_2]_0 - [M_2]}$	Analysis Carbon, %
(M <sub>2</sub> ) = Methyl methacrylate				
283	847	251.7	320	68.49
648	650	348	250	72.41
1145	352	342	127	77.09
(M <sub>2</sub> ) = Methyl acrylate				
1030	515	223	91	75.94
714	714	176	109	72.58
441	886	246	208	69.93
(M <sub>2</sub> ) = Butyl acrylate				
1035	344	216	55	80.09
550	549	160	88	75.67
228	686	106.7	110	72.36
(M <sub>2</sub> ) = Methacrylonitrile				
828	826	254	191	10.10
393	1177	334	403	12.49
393	1177	156	172.3	12.07
828	826	170	131.7	10.25
1311	436	169.7	87.0	8.14
(M <sub>2</sub> ) = Vinylidene chloride				
1158	387	306	47.5	15.95
663	662	240	84.8	28.34
291	870	84.1	46.0	32.92

<sup>a</sup> In millimoles.

Monomer reactivity ratios for the five systems studied are given in Table III.

It is of interest to compare these results with those obtained in the copolymerization of styrene with these same monomers. In Table IV, relative reactivities toward the styrene and butadiene

(9) (a) R. G. Fordyce, E. C. Chapin and G. E. Ham, *THIS JOURNAL*, **69**, 581 (1947); (b) R. G. Fordyce, *ibid.*, **69**, 1903 (1947); (c) R. G. Fordyce and G. E. Ham, *J. Polymer Sci.*, **3**, 891 (1948).

(10) W. V. Smith, *THIS JOURNAL*, **70**, 2177 (1948).

(11) F. T. Wall, R. E. Florin and C. J. Delbecq, *ibid.*, **72**, 4769 (1950).

(12) An attempt to copolymerize butadiene with methyl acrylate at 0°, using ultraviolet light and 2-azobisisobutyronitrile as a sensitizer gave no polymer, even after several days.

(13) Specifications for Government Synthetic Rubbers, Section E-1, Revised edition issued January 1, 1949 by the Reconstruction Finance Corporation, Office of Rubber Reserve.

(14) F. R. Mayo and F. M. Lewis, *THIS JOURNAL*, **66**, 1594 (1944).

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

(16) F. M. Lewis, C. Walling, W. Cummings, E. R. Briggs and F. R. Mayo, *THIS JOURNAL*, **70**, 1519 (1948).

TABLE III  
MONOMER REACTIVITY RATIOS FOR BUTADIENE ( $M_1$ ) IN  
EMULSION COPOLYMERIZATION AT 5°

$M_2$	$r_1$	$r_2$
Methyl methacrylate	$0.53 \pm 0.05$	$0.06 \pm 0.03$
Methyl acrylate	$.76 \pm .04$	$.05 \pm .02$
Butyl acrylate	$.99 \pm .07$	$.08 \pm .02$
Methacrylonitrile	$.36 \pm .07$	$.04 \pm .04$
Vinylidene chloride	$1.9 \pm .2$	$< .05$

TABLE IV  
COMPARISON OF PROPERTIES OF BUTADIENE AND STYRENE  
RADICALS IN COPOLYMERIZATION

Radical	Butadiene rel. react. 5°	$r_1 r_2$	Styrene rel. react. 60°	$r_1 r_2$
Monomer				
Butadiene	1.00	...	1.28 <sup>a</sup>	1.08
Styrene	0.72 <sup>a</sup>	1.08	1.00	..
Methyl methacrylate	1.89	0.032	1.9 <sup>b</sup>	0.24
Methyl acrylate	1.32	.038	1.34 <sup>b</sup>	0.14
Methacrylonitrile	2.78	.014	3.3 <sup>a</sup>	0.06
Vinylidene chloride	0.53	7.1	0.54 <sup>c</sup>	0.16

<sup>a</sup> From ref. (6). <sup>b</sup> From ref. (18). <sup>c</sup> F. R. Mayo, F. M. Lewis and W. F. Hulse, *THIS JOURNAL*, **67**, 1701 (1945).

radicals and  $r_1 r_2$  products are compared for the monomers reported here.

The table permits two generalizations.<sup>17</sup> First, since the  $r_1 r_2$  products in the butadiene systems are smaller than those involving styrene, and since the monomers in general belong to the electron acceptor class,<sup>15,18</sup> butadiene must be a better electron donor than styrene.

Second, the close similarity of the two reactivity series reinforces the conclusion,<sup>18</sup> that styrene and butadiene must lie very close together in reactivity. Since a similar correspondence has been found in chain transfer with mercaptans,<sup>19</sup> styrene serves as a convenient substitute for butadiene in oil phase polymerizations where polymerization of butadiene is inconveniently slow.

(17) The two radicals have, of course, been compared at different temperatures. However, unpublished experiments by the authors indicate that the change in monomer reactivity ratios in these butadiene systems in going from 5 to 60° is small.

(18) F. R. Mayo, F. M. Lewis and C. Walling, *THIS JOURNAL*, **70**, 1529 (1948).

(19) W. V. Smith, *ibid.*, **65**, 2064 (1943).

PASSAIC, N. J.

RECEIVED MAY 11, 1951

[CONTRIBUTION FROM THE IPATIEFF HIGH PRESSURE AND CATALYTIC LABORATORY, DEPARTMENT OF CHEMISTRY, NORTHWESTERN UNIVERSITY]

## Isomerization of Saturated Hydrocarbons. IX.<sup>1</sup> Isomerization of Ethylcyclopentane, 1,3-Dimethylcyclopentane and 1,1-Dimethylcyclopentane in the Presence of Aluminum Bromide. Synthesis of 1,1-Dimethylcyclopentane

BY HERMAN PINES, F. J. PAVLIK<sup>2</sup> AND V. N. IPATIEFF

The relative ease of the isomerization of ethylcyclopentane, 1,3-dimethylcyclopentane and 1,1-dimethylcyclopentane to methylcyclohexane was studied. Under certain experimental conditions these hydrocarbons do not undergo ring expansion when subjected to aluminum bromide-hydrogen bromide unless traces of alkyl halides are added or when the reagents are exposed to ultraviolet light. In the presence of small amounts of oxygen, aluminum bromide *per se* acts as an isomerizing catalyst. The isomerization is inhibited by the presence of benzene. Ethylcyclopentane isomerizes more readily than 1,3-dimethylcyclopentane and the latter more readily than 1,1-dimethylcyclopentane; these results can be interpreted on the basis of the ionic chain mechanism. The synthesis of 1,1-dimethylcyclopentane is described.

It has previously been shown that under certain controlled conditions aluminum bromide-hydrogen bromide did not cause isomerization of *n*-butane to isobutane<sup>3</sup> or methylcyclopentane to cyclohexane<sup>4</sup> unless traces of olefins or alkyl halides were present.

It was also shown that ultraviolet light<sup>5</sup> promotes the isomerization of methylcyclopentane to cyclohexane in the presence of aluminum bromide-hydrogen bromide and that aluminum bromide in the presence of oxygen<sup>6</sup> and in the absence of hydrogen bromide causes a similar rearrangement. It was further shown<sup>1,7</sup> that benzene inhibits isomerization.

In order to explain the function of the various promoters an ionic mechanism was proposed<sup>4,8</sup> in which it was assumed that the alkyl halides, added as such or formed *in situ*, acted as chain initiators.

For methylcyclopentane a primary carbonium ion was assumed responsible for ring expansion. In the case of ethylcyclopentane the expansion of the five-membered ring to a six-membered ring would involve, according to the above ionic mechanism, a secondary carbonium ion. Since the latter is usually formed more readily than a primary carbonium ion such isomerization should proceed with greater ease.

In the case of 1,3-dimethylcyclopentane although the chance for formation of a tertiary carbonium ion as the probable primary step in the reaction is twice that for ethylcyclopentane it was assumed that the isomerization would proceed less readily than in the case of ethylcyclopentane because of the necessary formation of a primary carbonium ion for ring expansion.

(8) H. S. Bloch, H. Pines and L. Schmerling, *THIS JOURNAL*, **68**, 153 (1946).

(1) For paper VIII of this series see H. Pines, E. Aristoff and V. N. Ipatieff, *THIS JOURNAL*, **72**, 4304 (1950).

(2) Universal Oil Products Company Predoctorate Fellow 1949-1951.

(3) H. Pines and R. C. Wackher, *THIS JOURNAL*, **68**, 595, 2518 (1946).

(4) H. Pines, B. M. Abraham and V. N. Ipatieff, *ibid.*, **70**, 1742 (1948).

(5) H. Pines, E. Aristoff and V. N. Ipatieff, *ibid.*, **72**, 4055 (1950).

(6) H. Pines, E. Aristoff and V. N. Ipatieff, *ibid.*, **71**, 749 (1949).

(7) J. M. Mavity, H. Pines, R. C. Wackher and J. A. Brooks, *Ind. Eng. Chem.*, **40**, 2374 (1948).