

ganic bromide to inorganic iodide, b is the initial concentration of iodide, and z is the fraction of the iodide which has reacted in the time t . From the linear plot of this equation the best value of the velocity constant k can be chosen. All the bromides yielded satisfactory straight lines, and successive runs on the same compound yielded constants within 5% of the mean. Most of the runs were carried to more than 75% of completion.

The table gives the data for a sample run in

TABLE II

RATE OF REACTION BETWEEN 1-BROMO-4,4-DIMETHYLPENTYNE-2 AND POTASSIUM IODIDE IN ACETONE SOLUTION AT 25°

Initial molarity of potassium iodide, 0.01044; of 1-bromo-4,4-dimethylpentene-1, 0.01530; initial titer of potassium iodide (determined on blank) 34.80 cc.; $M = 1.466$.

Time in minutes	Titer	z	$\log \frac{M-z}{M(1-z)}$
2.52	22.80	0.345	0.0673
4.26	18.60	.466	.1065
6.00	16.35	.530	.1331
9.00	14.40	.586	.1613
10.02	13.50	.612	.1766
17.52	9.85	.717	.2566
25.02	8.90	.744	.2841

which the rate of reaction of 1-bromo-4,4-dimethylpentene-2 with potassium iodide was measured. The first and last points on the plot of the logarithmic quantity against time are below the straight line determined by the other points. This is not typical of the runs. The slope of the straight line yields the value $k = 5.35$ for the bimolecular velocity constant of the reaction.

Summary

The rates of reaction between potassium iodide in acetone and some organic bromides have been measured in order to gain an insight into the nature of the hindrance to displacement reactions in neopentyl halides. From the fact that 1-bromo-4,4-dimethylpentene-2 is not hindered in comparison to 1-bromo-heptyne-2 it is concluded that the "neopentyl effect" is not capable of transmission through an unsaturated linkage and is hence not a chemical but a steric effect. A consideration of the mechanism of displacement reactions in terms of models and the reactivities of the compounds studied are in agreement with this conclusion.

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[CONTRIBUTION FROM THE RESEARCH LABORATORY OF PHYSICAL CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY, No. 488]

Vapor Pressures and Critical Constants of Isobutene

BY JAMES A. BEATTIE, HENRY G. INGERSOLL AND WALTER H. STOCKMAYER

In previous publications¹ determinations of vapor pressures and critical constants of ethane, propane, *n*-butane, and *n*-heptane have been given. The apparatus and method have been published elsewhere.² In the present paper data on isobutene are presented. The compressibility bomb with a glass liner² was used.

The isobutene was obtained from the M. W. Kellogg Company through the courtesy of Dr. Manson Benedict. It was prepared by the dehydration of isobutyl alcohol over activated alumina followed by fractionation. We distilled the sample several times to remove permanent gases.

Vapor Pressures

The vapor pressure of isobutene has been measured from -79 to +22° by Coffin and Maass,³

(1) For the last report on this work see J. A. Beattie, G. J. Su, and G. L. Simard, *THIS JOURNAL*, **61**, 924-925 (1939).

(2) J. A. Beattie, *Proc. Am. Acad. Arts Sci.*, **69**, 389-405 (1934).

(3) C. C. Coffin and O. Maass, *Trans. Roy. Soc. Canada*, [3] III, **21**, 33-40 (1927).

from 36° to the critical point by Scheeline and Gilliland,⁴ and from -57 to 0° by Lamb and Roper.⁵

In Table I are given the results of our measurements made in the compressibility apparatus. The variation of vapor pressure with vapor volume affords a test of the purity of the sample. The small increase of vapor pressure with decrease of vapor volume indicates that the amount of permanent gas present was entirely negligible and that the effect of the condensable impurity present was slightly greater than the reproducibility of the measurements.

In Table II is given the comparison of the observed vapor pressures with those computed from a two-constant equation. The equation yields a value at 0° (an extrapolation of 25°) in excellent

(4) H. W. Scheeline and E. R. Gilliland, *Ind. Chem. Eng.*, **31**, 1050-1057 (1939).

(5) A. B. Lamb and E. E. Roper, *THIS JOURNAL*, **62**, 806-814 (1940).

TABLE I

EFFECT OF VARIATION IN VAPOR VOLUME ON VAPOR PRESSURE OF THE ISOBUTENE SAMPLE

Temp. (°C. Int.)	30	50	75	100	125
Vapor vol. (cc.) ^a	Vapor pressure, normal atmospheres				
100	3.446		10.853	18.075	
80	3.443	5.974			
60	3.444	5.974	10.854	18.073	
40		5.974	10.857	18.077	28.397
20		5.975	10.859	18.085	28.410
10		5.979	10.865	18.092	28.415
5		5.979	10.869	18.091	28.419
0.5			10.868	18.093	28.419
0.25		5.979			
Highest <i>p</i> - lowest <i>p</i>	0.003	0.005	0.016	0.020	0.022
Average <i>p</i>	3.444	5.976	10.861	18.084	28.412

^a Approximate.

TABLE II

VAPOR PRESSURE OF ISOBUTENE

$$\log_{10} p(\text{atm.}) = 4.3759_2 - (1163.34/T) \quad (T = t^\circ\text{C.} + 273.13)$$

Temp. (°C. Int.)	Vapor pressure (normal atm.)	
	Obsd.	Obsd. - calcd.
0	1.301 ^a	-0.007
30	3.444	- .009
50	5.976	+ .010
75	10.86	+ .04
100	18.08	- .04
125	28.41	- .03

^a From equation of Lamb and Roper.⁵

agreement with that given by the equation of Lamb and Roper. The agreement of our results with those of Coffin and Maass, and of Scheeline and Gilliland is fair.

Critical Constants

The results of the measurements of the compressibility of isobutene in the critical region are

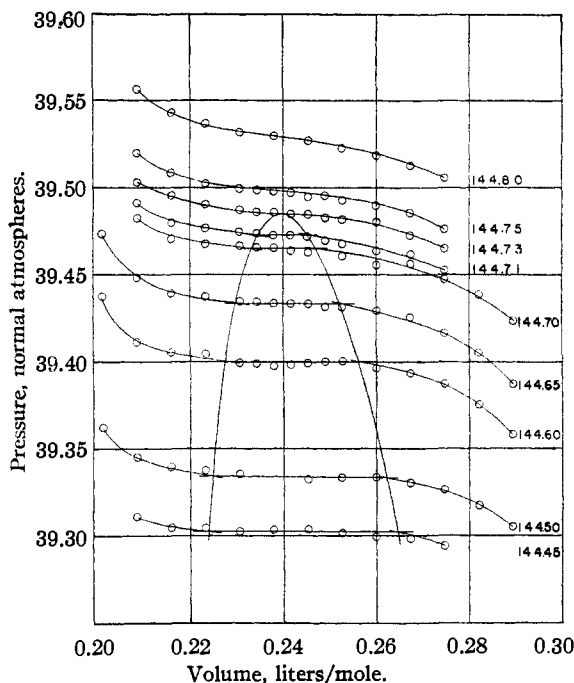


Fig. 1.—Isotherms of isobutene in the critical region. The radius of each circle is 0.002 atm.

given in Table III. The isotherms are plotted in Fig. 1 and the critical constants derived from the plot are listed at the bottom of Table III. In

TABLE III

ISOTHERMS OF ISOBUTENE IN THE CRITICAL REGION

Molecular weight of (CH₃)₂C=CH₂ = 56.0616

Temp., °C. (Int.)	144.45	144.50	144.60	144.65	144.70	144.71	144.73	144.75	144.80
Volume liter/mole									
Density mole/liter									
Pressure, normal atmospheres									
0.2891	3.459	39.3050	39.3585	39.3870	39.4235				
.2819	3.547		39.3175	39.3755	39.4055	39.4390			
.2746	3.642	39.2945	39.3270	39.3870	39.4170	39.4475	39.4530	39.4650	39.4760
.2673	3.741	39.2985	39.3300	39.3940	39.4260	39.4565	39.4615	39.4725	39.4850
.2600	3.846	39.3000	39.3335	39.3960	39.4290	39.4560	39.4635	39.4800	39.4900
.2527	3.957	39.3020	39.3330	39.4005	39.4315	39.4610	39.4680	39.4815	39.4925
.2491	4.014			39.4000	39.4320		39.4695	39.4830	39.4950
.2454	4.075	39.3040	39.3320	39.3995	39.4335	39.4625	39.4720	39.4845	39.4945
.2418	4.136			39.3985	39.4335	39.4640	39.4725	39.4845	39.4970
.2381	4.200	39.3035		39.3975	39.4340	39.4650	39.4725	39.4855	39.4975
.2345	4.264			39.3990	39.4340	39.4650	39.4740	39.4860	39.4985
.2308	4.333	39.3025	39.3355	39.3995	39.4350	39.4670	39.4745	39.4870	39.4995
.2236	4.472	39.3045	39.3375	39.4045	39.4370	39.4675	39.4770	39.4905	39.5020
.2163	4.623	39.3050	39.3395	39.4055	39.4395	39.4705	39.4800	39.4955	39.5085
.2090	4.785	39.3110	39.3450	39.4115	39.4485	39.4825	39.4915	39.5030	39.5200
.2017	4.958		39.3620	39.4370	39.4735				

Critical constants from Fig. 1: *t*_c = 144.73 ± 0.05 °C. (Int.); *p*_c = 39.48 ± 0.05 normal atm.; *v*_c = 0.240 liter/mole (4.28 cc./g.); *d*_c = 4.17 mole/liter (0.234 g./cc.). The uncertainty in the critical volume and density is 1%.

Table IV the critical constants obtained in this investigation are compared with the results of other workers. The agreement of our values with those of Benedict,⁶ who used the disappearance of the meniscus method, is striking.

TABLE IV

COMPARISON OF THE CRITICAL CONSTANTS OF ISOBUTENE FROM THIS INVESTIGATION WITH THE VALUES OF OTHER AUTHORS

Source	t_c , °C. (Int.)	p_c (normal atm.)	d_c (g./cc.)
This investigation	144.73 ± 0.05	39.48 ± 0.05	0.234 ± 0.002
Coffin and Maass ¹	143.5		
Scheeline and Gilliland ²	148.9	39.7	
M. Benedict ⁶	144.6 ± 0.6	39.5 ± 0.2	

The prosecution of this work was greatly aided by a fellowship from the Polymerization Process Corporation. We wish to thank the M. W. Kellogg Company for the gift of the isobutene.

(6) Manson Benedict, private communication.

Summary

The vapor pressure of isobutene was measured from 30 to 125°. The equation $\log_{10} p(\text{atm.}) = 4.3759_2 - (1163.34/T)$ represents the results well and also computes a vapor pressure at 0° in good agreement with that measured by Lamb and Roper.

The critical constants of isobutene determined by the compressibility method are: $t_c = 144.73 \pm 0.05^\circ\text{C. (Int.)}$; $p_c = 39.48 \pm 0.05$ normal atmosphere; $v_c = 0.240$ liter/mole (4.28 cc./g.); $d_c = 4.17$ mole/liter (0.234 g./cc.). The uncertainty in the critical volume and density is 1%. The critical pressure and temperature given above are in excellent agreement with those determined by Benedict, who used the disappearance of the meniscus method.

CAMBRIDGE, MASS.

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The Compressibility of and an Equation of State for Gaseous Isobutene

BY JAMES A. BEATTIE, HENRY G. INGERSOLL AND WALTER H. STOCKMAYER

In earlier papers from this laboratory¹ the compressibilities of methane, ethane, propane, *n*-butane, and *n*-heptane have been reported. The properties of the last four substances have been measured in the same compressibility apparatus which has been described elsewhere.² We have determined vapor pressures and critical constants of isobutene using a bomb with the glass liner.² The compressibility of the same isobutene sample was then measured from 150 to 275° and to densities of 1.5 to 2 times the critical.

The rate of polymerization of isobutene in a glass-lined bomb above 330° has been measured by Krauze, Nemtsov and Soskina.³ Calculations made from their equations extrapolated to lower temperatures showed that in the time required for a complete compressibility run at one temperature—about ten hours—the effect of the polymerization at 225° would be of the order of the reproducibility of the compressibility measurements. Actually we measured the 250 and 275°

isotherms before the effect of the polymerization became serious. As with the other hydrocarbons we measured the pressure along each isotherm from the lowest to the highest density and then repeated some of the measurements at the lower densities as the pressure was decreased. In Table I are given the pressures for the lowest density—1 mole/liter—before and after each set of isotherms as well as the pressure at 150° before and after the complete series of runs. It will be seen that up to 250° the effect of polymerization is small, while at 275° it may have affected the results by as much as 0.5%.

The constants of the Beattie-Bridgeman equation of state for isobutene determined from the compressibility measurements up to the critical density (4.17 mole/liter) are given in Table II and a comparison of the calculated with the observed pressures in Table III. The variation of the *c* constant of the equation of state with density, which has been noticed for other substances, is quite evident in the case of isobutene. The change in curvature of the isometrics from negative at low density to positive at high density takes place at a density between 3.5 to 4.0 mole/

(1) For the last report on this work see J. A. Beattie, G.-J. Su, and G. L. Simard, *THIS JOURNAL*, **61**, 926-927 (1939).

(2) J. A. Beattie, *Proc. Am. Acad. Arts Sci.*, **69**, 389-405 (1934).

(3) M. V. Krauze, M. S. Nemtsov and E. A. Soskina, *J. Gen. Chem.*, **5**, 382-387 (1935).