In all cases, zero-point titrations were made in order to avoid as many extraneous errors as possible. The decompositions were carried into the 50-80% range, and the results, as C_0/C, were plotted *versus* time on semilogarithmic paper. Three or more experimental points were employed to establish the rate curve for each initial concentration, and the deviations from this curve rarely exceeded ±1%. Experimental points often were titrated in duplicate; the deviation rarely exceeded ±0.2%. The greatest uncertainty was evidently the occasional lack of reproducibility of the rate curves; sometimes the variation would be as high as 5%, particularly for initial concentrations of peroxide below 0.03 *M*.

Table VI lists representative rate constants for typical runs with three peroxides and Table IV presents the rate constants for sixteen different peroxides extrapolated to zero peroxide concentration.

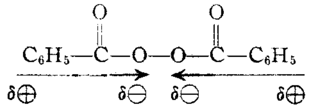
Acknowledgment.—The authors thank Swift and Company for a grant supporting this research.

Summary

1. It is possible substantially to eliminate the bimolecular induced chain process in the thermal decomposition of benzoyl peroxide at 80° in dioxane solution by adding 0.2 *M* 3,4-dichlorostyrene, which is the best of thirty-nine inhibitors tested.

2. In the *bimolecular* induced chain decomposition, electron-attracting substituents in the peroxide accelerate reaction. Stabilization of the transition state by polar resonance structures involving transfer of an electron from a solvent radical to the peroxide seems to be the dominant factor governing the change of rate with structure.

3. In the *unimolecular* spontaneous thermal decomposition, on the other hand, electron-attracting substituents retard the reaction and electron-repelling groups accelerate. The data on sixteen different *m*- and *p*-substituted benzoyl peroxides fit the Hammett equation closely. Here the most important influence governing the rate seems to be the magnitude of the coulombic repulsion between the opposing dipoles at the two ends of the molecule.



$$\underset{\delta\oplus}{C_6H_5}-\overset{\overset{\displaystyle O}{\|}}{C}\xrightarrow{\quad}\underset{\delta\ominus}{O}-\underset{\delta\ominus}{O}\xleftarrow{\quad}\overset{\overset{\displaystyle O}{\|}}{C}-\underset{\delta\oplus}{C_6H_5}$$

CAMBRIDGE, MASS. RECEIVED MARCH 22, 1950

[CONTRIBUTION NO. 82 FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF TENNESSEE]

The Dipole Moments of the 1,2-Dibromopropenes

BY HILTON A. SMITH AND LLOYD E. LINE, JR.

While the preparation of 1,2-dibromopropene is reported several times in the literature, only one attempt to separate the two geometrical isomers and to assign *cis* and *trans* structures to them is recorded. Van Risseghem[1] obtained a mixture of isomers by treating 1,2,2-tribromopropane with sodium phenylate in alcoholic solution. He found it impossible to separate the two isomers by fractionation procedures since isomerization took place at the boiling point of the mixture (125–133°). He did separate them by means of an azeotropic distillation with propanol, the boiling points of the two azeotropes being 95.75 and 97.05°. The isomers were recovered from the propanol solutions, and the *cis* structure suggested for the higher-boiling isomer since it showed the greater speed of dehydrobromination with potassium hydroxide.

It seemed worthwhile to check this assignment by a reliable physical method. For this reason, the two isomers were obtained, and their dipole moments measured. The results are reported here.

Experimental

Materials.—The dibromopropenes were obtained as a mixture of *cis* and *trans* isomers from the Columbia Organic Chemicals Company, Inc., of Columbia, S. C. According to information received from this company, the mixture was prepared by dehydrohalogenation of 1,2,2-tribromopropane. The materials were stored over anhydrous potassium carbonate prior to use. They were separated by fractional distillation over anhydrous potassium carbonate at about 30 mm. pressure in an eight-foot Vigreux column. The plentiful lower boiling isomer was redistilled, but the higher-boiling isomer was used without further purification. A fractionation curve is shown in Fig. 1, while the physical properties of the isomers are given in Table I.

TABLE I

PHYSICAL PROPERTIES OF THE 1,2-DIBROMOPROPENES

Isomer, boiling		Lower, *trans*	Higher, *cis*
Distillation range	°C.	40.9 ± 0.1	51.4 ± 0.2
	Mm.	28	28
d^{30}_4		1.9743	1.9900[a]
n^{20}_D		1.5326	1.5282
n^{30}_D		1.5275	1.5236

[a] Corrected to time of distillation.

Reagent grade (thiophene-free) benzene was fractionated through a five-foot helix-packed distillation column before use as a solvent for the determination of the dielectric constant.

Apparatus and Methods.—Because of the tendency toward isomerization[1] each benzene solution was made up and its capacitance determined as quickly as possible after collection of each sample from the still. For the first run on the higher boiling isomer, the individual samples were weighed, and the benzene solutions made from them also weighed. This caused a delay of several hours between time of collection of each sample and measurement of the dielectric constant. Subsequently, the variation in density of benzene solutions of the dibromopropenes with concentration was established. Figure 2 shows a plot of this variation. It will be noted that the points for solutions of the two isomers fit essentially the same straight line.

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[1] H. Van Risseghem, *Bull. soc. chim. Belg.*, **28**, 376 (1919).

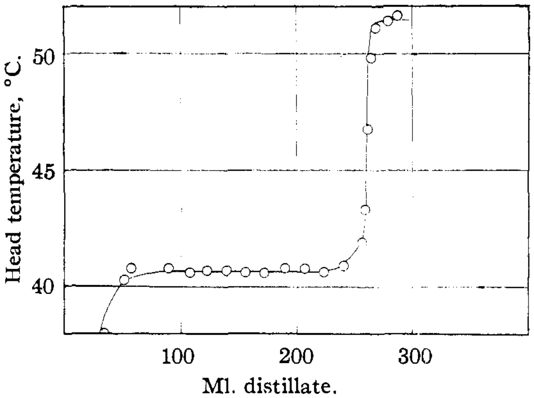

Fig. 1.—Low pressure (30 mm.) fractional distillation of *cis*- and *trans*-1,2-dibromopropenes.

The equations for the solutions of the two isomers as calculated by the method of least squares are

$$\text{higher boiling isomer, } d^{30}_4 = 1.256f_2 + 0.8679$$
$$\text{lower boiling isomer, } d^{30}_4 = 1.240f_2 + 0.8682$$

where d is the density of the solution and f_2 is the mole fraction of the bromopropene. For the low boiling isomer and for the second run with the high-boiling material, the samples were mixed with benzene immediately after collection, and their dielectric constants determined. This involved a delay of not more than thirty minutes. The densities were subsequently determined, and solute mole fractions calculated from the equations given above.

The capacitances were measured in a brass cell immersed in a water-bath held at 30 ± 0.1° when the measurements were made. The apparatus was of the heterodyne beat type, with a brass cell containing a 50 $\mu\mu$f condenser which had been split. By means of an external control, this condenser could be used either as a whole or in part. Dielectric constants were thus obtained directly as the ratio of capacitance differences in the medium and in air, and any cell and lead capacitances were eliminated.[2] A General Radio, Model 722-D Precision condenser was used. All solutions were colorless and clear throughout measurements of capacitance and density.

Densities were determined after the capacitance measurements using Sprengel pycnometers and a water-bath maintained at 30 ± 0.01°. The density and dielectric constant of the benzene solvent used for each of the three series of measurements were determined independently for each set of measurements.

Experimental Calculations and Results

The dipole moments were calculated from the solute mole fractions (f_2), the dielectric constants (ϵ), and the solution densities (d) using standard equations.[2] The experimental results are summarized in Table II. It was found that values of P_2 for mole fractions of around 0.01 or less were erratic, and these are not included in the tabulation. In obtaining P_∞ for the higher boiling isomer, the data from both runs were plotted on the same graph. The value of 119.5 obtained in the first series was omitted, since it is obviously in error. The values of the molar refraction (MR_D), the molar polarization (P_∞), and the dipole moment (μ) for each isomer are listed in Table III.

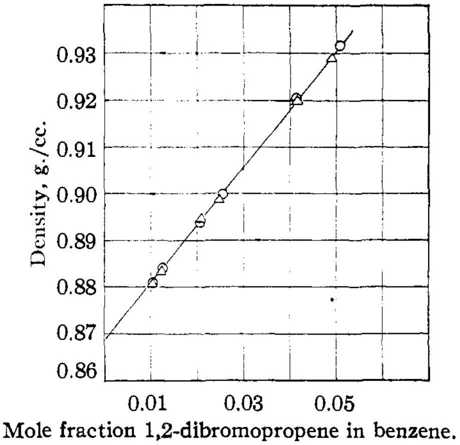

Fig. 2.—Variation of density with mole fraction of 1,2-dibromopropene in benzene: O, *cis*; △, *trans*.

TABLE II

DIELECTRIC CONSTANTS, DENSITIES AND MOLAR POLARIZATIONS OF BENZENE SOLUTIONS AT 30°

f_2	ϵ	d^{30}_4	P_2, cc./mole
1,2-Dibromopropene, Higher Boiling Isomer, First Run			
0.051081	2.5765	0.9318	108.7
.041517	2.5210	.9205	108.7
.025400	2.4460	.8997	119.5
.020697	2.4038	.8938	111.7
.000000	2.2860	.8679	27.004 (= P_1)
1,2-Dibromopropene, Higher Boiling Isomer, Second Run			
0.041284	2.5272	0.9198	108.3
.032849	2.4761	.9091	107.6
.024857	2.4328	.8991	108.7
.016992	2.3846	.8892	105.5
.000000	2.2953	.8679	27.141 (= P_1)
1,2-Dibromopropene, Lower Boiling Isomer			
0.041071	2.3469	0.9191	53.4
.034753	2.3395	.9113	54.6
.033692	2.3374	.9099	54.4
.025003	2.3234	.8991	54.8
.016726	2.3119	.8889	56.9
.000000	2.2820	.8683	26.931 (= P_1)

TABLE III

MOLAR POLARIZATIONS, MOLAR REFRACTIONS AND DIPOLE MOMENTS MEASURED AT 30° IN BENZENE SOLUTION

Compound		MR_D, cc./mole	P_∞, cc./mole	μ, Debye units
1,2-Dibromopropene isomer	higher b.	30.72	108.6	1.97
	lower b.	31.15	58.0	1.16

Discussion

The dipole moments of the two isomeric 1,2-dibromopropenes as given in Table III indicate that the higher boiling isomer is undoubtedly the *cis* form. This confirms the assignments of Van Risseghem on the basis of reaction rates.[1]

It is interesting to compare the moments for the dibromopropenes (1.97 and 1.16) with those of the 1,2-dichloro- (1.89 and 0) and 1,2-dibromoethylenes (1.35 and 0)[3] and with the 1,2-dichloropro-

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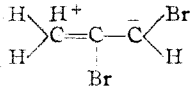
(2) C. P. Smyth, "Dielectric Constant and Molecular Structure," Chemical Catalog Company, Reinhold Publishing Corp., New York, N. Y., 1931, p. 59.

(3) J. Errera, *Physik. Z.*, **27**, 764 (1926).

penes (2.2 and 0.84).[4] The fact that the *trans* forms of the propenes have as high moments as found must be due to interactions involving the methyl group, since the moments of the *trans* forms of the 1,2-dichloro- and 1,2-dibromoethylenes are both zero. Presumably charge-separated resonance isomers such as the following are involved



The *cis*-1,2-dibromopropene has a lower dipole moment than the corresponding chloropropene, while the result is reversed for the *trans* forms. The former result is in line with the fact that *cis*-1,2-dibromoethylene has a moment (1.35) lower than that of the corresponding dichloroethylene (1.89). The latter result could be explained if each isomer were contaminated with the other, and this is a possibility in view of the known isomerization. However, the distillations were carried out at low pressure and not far from room temperature. Since Van Risseghem showed that no isomerization of either form occurred after standing four days at room temperature in the absence of air, it seems reasonable to suppose that little isomerization took place in any part of the column during the collection of the sample. Moreover, if isomerization did occur, the lower boiling (*trans*) isomer should still have been pure. There was no indication that any appreciable isomerization occurred during the period of capacitance measurements.

An explanation of this anomaly may lie in the following. The difference (0.54) between the dipole moments of *cis*-dichloroethylene (1.89) and *cis*-dibromoethylene (1.35) represents the direct lowering of the dipole moment when bromine is substituted for chlorine in a *cis*-1,2-dihaloethylenic compound, for here no resonance into charge-separated isomers like that shown above is possible. The difference (0.32) in moment between the *trans*-dichloropropene (0.84) and the *trans*-dibromopropene (1.16) must be due to the increase in contribution of resonance isomers when bromine is substituted for chlorine in the 1,2-dihalopropene molecule, for the simple vector moments of the halogens in these compounds must cancel.

When one substitutes bromine for chlorine in the *cis*-1,2-dihalopropenes both the direct lowering of the moment as found in the *cis*-dihaloethylenes and the increase in moment due to resonance as exhibited in the *trans*-1,2-dihalopropenes should appear. The net decrease ($0.54 - 0.32 = 0.22$) is in agreement with the experimentally observed quantity ($2.20 - 1.97 = 0.23$). Exact agreement is probably fortuitous.

Summary

The isomeric 1,2-dibromopropenes have been obtained in a pure state, and their dipole moments have been measured. The results confirm the assignment of the *cis* structure to the higher boiling isomer. The moments have been compared with those of the corresponding dichloro compounds, and with the dichloro- and dibromoethylenes, and the differences discussed.

Knoxville, Tennessee Received May 29, 1950

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[4] W. H. King and H. A. Smith, This Journal, **72**, 3459 (1950); *cf.* H. A. Smith and W. H. King, *ibid.*, **70**, 3528 (1948).

[Contribution of the Research & Development Branch, Office of Synthetic Liquid Fuels, Bureau of Mines]

Studies of the Fischer–Tropsch Synthesis. VIII.[1] Surface Area and Pore Volume Studies of Iron Catalysts

By W. Keith Hall, William H. Tarn and Robert B. Anderson

This paper reports the changes in surface area and pore volume during the reduction of two widely different iron catalysts, a precipitated Fe_2O_3–CuO–K_2CO_3 catalyst and a fused Fe_3O_4–MgO–K_2O catalyst. The studies provide information as to the nature of iron catalysts at the start of the Fischer–Tropsch synthesis, as well as data pertinent to the mechanism of reduction. Previous papers have presented data describing the surface area and pore volumes of cobalt Fischer–Tropsch catalysts.[2,3,4]

Phase relations of the iron–oxygen system have been presented by Kelly,[5] and the thermodynamics of the reduction of iron oxide were discussed by Emmett and Shultz.[6] Udy and Lorig,[7] Meyer[8] and Tennenbaum and Joseph[9] have reported data pertinent to the mechanism of the reduction, and Brunauer and Emmett[10] have reported changes in surface area that occur

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[1] Part VII of this series Anderson, Shultz, Seligman, Hall and Storch, This Journal, **72**, 3502 (1950).

[2] Anderson, Hall, Hewlett and Seligman, *ibid.*, **69**, 3114 (1947).

[3] Anderson, Hall and Hofer, *ibid.*, **70**, 2465 (1948).

[4] Anderson, Hall, Krieg and Seligman, *ibid.*, **71**, 183 (1949).

[5] Kelly, Bureau of Mines, Bulletin 296, Iron Oxide Reduction Equilibria.

[6] Emmett and Shultz, This Journal, **52**, 4268 (1930); **55**, 1376 (1933).

[7] Udy and Lorig, *Metals Technology*, T. P. 1509 (1942).

[8] Meyer, K. W. I. Band 10 (1928), "Von die Reduktionsgeschwindegheit von Eisenerzen in Strömenden Gasen."

[9] Tennenbaum and Joseph, *AIMME Transactions*, **135**, (1939).

[10] Brunauer and Emmett, This Journal, **59**, 310, 1553, 2682 (1937); **62**, 1732 (1940).