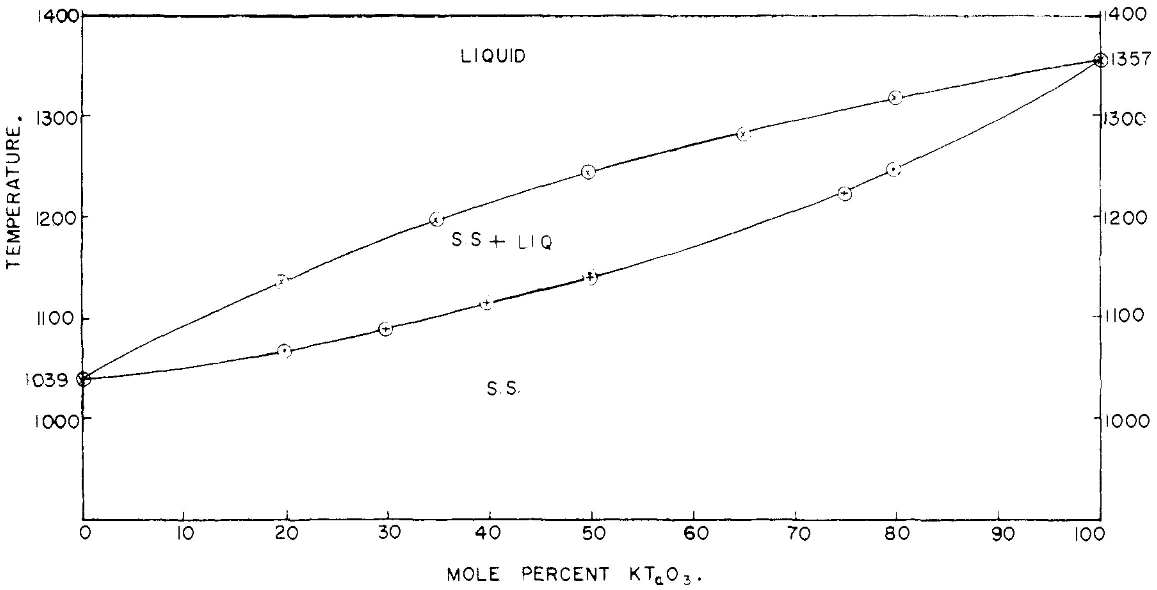

Fig. 2.—Phase diagram of system $KNbO_3$–$KTaO_3$: ⊗, cooling curves; ⊕, conductivity curves; ⊙, heating curves.

ture indicated that there was no low temperature exsolution.

The melting point of pure potassium tantalate as determined in this study was found to be 1357 ± 3°.

The method of conductivity analysis results in a clearly defined solidus transition. The data agree with thermal analysis measurements to within ±3°. Because of the definite change in slope and time independence, the new technique is apparently superior in defining the solidus.

Acknowledgment.—The authors wish to acknowledge the assistance given them by Mr. G. Burns who prepared the ceramics, Mr. K. Asai who prepared the potassium salts, Mr. M. Berkenblit for preparation of the charges and Miss M. Berry for X-ray analysis.

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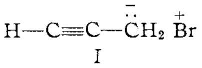
The Electric Moments of Some Allylic Compounds and of Some Simple Halides

BY MAX T. ROGERS AND MORTON B. PANISH

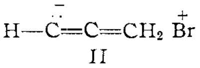
RECEIVED MARCH 29, 1955

A study of the electric moments of some propargyl compounds[1] indicated that the acetylenic group is electron-attracting; to account for the electric moments of the propargyl halides it was proposed that the C–X bond moments in the halides were lowered below the normal values through the contribution of structures such as I and II.



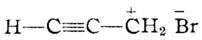
$\mathrm{H{-}C{\equiv}C{-}\overset{\overset{-}{\cdot\cdot}}{C}H_2\ \overset{+}{Br}}$

I



$\mathrm{H{-}\overset{\overset{-}{\cdot\cdot}}{C}{=}C{=}CH_2\ \overset{+}{Br}}$

II



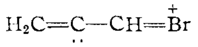
$\mathrm{H{-}C{\equiv}C{-}\overset{+}{C}H_2\ \overset{-}{Br}}$

III

Since analogous structures may be written for allylic compounds, the electric moments of several have been investigated to determine whether they make an appreciable contribution to the normal states of allylic compounds. It is also of interest to find out whether or not structures such as III, which electric moment data indicate are not important in propargyl derivatives, are significant in the allylic series. We have, therefore, measured the electric moments of allyl bromide, allyl iodide, allyl cyanide, allylamine, allyl ethyl ether and benzylaminein benzene solution at 25°. The moments of bromoallene and *trans*-1-bromopropene-1 in benzene solution are also reported here and redeterminations of the moments of *sec*-butyl chloride, cyclohexyl chloride and cyclohexyl bromide have been made. Values have been reported previously[2] for the above three compounds and for allyl bromide.

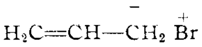
Results

The electric moment of bromoallene (1.50) is about equal to those of bromobenzene[2] (1.55) and vinyl bromide[2] (1.44). It might be expected that resonance with structures such as IV would be about equal in importance in bromoallene and vinyl bromide and both moments are found to be about 0.5 below that of *n*-propyl bromide. It is a coincidence that bromoallene and its isomer, 3-bromopropyne, have identical electric moments so that all mixtures of these substances show the same molar polarization.[1]



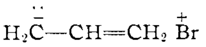
$\mathrm{H_2C{=}\underset{\underset{-}{\cdot\cdot}}{C}{-}CH{=}\overset{+}{Br}}$

IV



$\mathrm{H_2C{=}CH{-}\overset{-}{C}H_2\ \overset{+}{Br}}$

V



$\mathrm{H_2\overset{\overset{\cdot\cdot}{-}}{C}{-}CH{=}CH_2\ \overset{+}{Br}}$

VI

The observed electric moments of allyl bromide, iodide and cyanide agree within experimental error

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[1] M. T. Rogers and M. B. Panish, THIS JOURNAL, **77**, 3684 (1955).

[2] L. G. Wesson, "Tables of Electric Dipole Moments," The Technology Press, Cambridge, Mass., 1948.

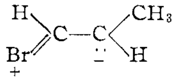
TABLE I

EMPIRICAL CONSTANTS, MOLAR REFRACTIONS, MOLAR POLARIZATIONS AND DIPOLE MOMENTS

Substance	ϵ_1	a	v_1	b	P_2	MR_D	$\mu_{obsd.}$	$\mu_{calcd.}$
Bromoallene	2.2706	3.150	1.14470	−0.743	69.58	22.88	1.50	..
Allyl bromide	2.2725	4.425	1.14460	−0.656	91.01	23.60	1.82	1.85
Allyl iodide	2.2725	3.697	1.14440	−1.213	83.36	29.73	1.62	1.74
Allyl cyanide	2.2725	16.13	1.14470	+0.090	262.0	19.84	3.44	3.46
Allyl ethyl ether	2.2727	2.23	1.14490	+0.130	65.17	26.41	1.37	1.26
Allylamine	2.2722	2.14	1.14490	+0.150	54.42	19.17	1.31	1.32
Benzylamine	2.2710	2.75	1.14480	−0.160	73.23	34.35	1.38	1.32
trans-1-Bromopropene-1	2.2706	3.78	1.14490	−0.656	81.56	23.19	1.69	1.66
sec-Butyl chloride	2.2738	5.56	1.14494	+0.002	113.27	25.58	2.07	..
Cyclohexyl chloride	2.2725	6.41	1.14470	−0.190	130.2	32.61	2.18	..
Cyclohexyl bromide	2.2725	6.909	1.14375	−0.783	138.8	35.82	2.24	..

with the calculated values shown in Table I. These were computed by vectorial addition of the propylene moment (0.4) to that of the corresponding saturated compound; it was assumed that the propylene moment lies along the bond joining the saturated and unsaturated carbon atoms and that all angles are tetrahedral. The observed values for allylamine, benzylamine and allyl ethyl ether also agree with the calculated moments within the experimental error (0.1 *D*); the moments of toluene and propylene are equal so the calculated values for allylamine and benzylamine are equal. It may be noted that the moments of benzyl bromide[1] and allyl bromide are nearly equal, also. These results do not suggest that there is any important contribution from structures of type V and VI in any of the substances studied or, at least, an equal contribution from structures of type III must be present. The acetylenic group appears, therefore, to be a more powerful electron-acceptor than the ethylenic group.[1]

The electric moments of *cis*- and *trans*-1-chloropropene (1.71 and 1.97) have been measured in the vapor state[3] and in solution,[4] and of *cis*-1-bromopropene (1.57) in benzene solution.[5] These moments differ from those calculated by vector addition of the propylene moment and a mesomeric moment to that of propyl chloride or bromide, when the same mesomeric moment is used as is found in the corresponding vinyl halide. The deviations are removed if the mesomeric moment is reduced by one-half in making calculations for the 1-halopropenes.[3,5] Such a reduction might result from a reduced contribution of structures of type VII in the halopropenes. However, the moment of *trans*-1-bromopropene found here (1.69) agrees well with the value 1.71 calculated by vector addition of the mesomeric moment 0.70 (from vinyl bromide), the propylene moment 0.40, and the propyl bromide moment, 1.95. Although the material used was probably not pure *trans* isomer, the experimental dipole moment would be raised to only 1.75 by the presence of one-third *cis* isomer. It is, however, possible that the moment obtained in benzene solution is lower than the gas moment just as the moment reported for *cis*-1-chloropropene in solution[4] is 0.2 *D* lower than that found in the gas.[3]



VII

Our values for the electric moments of cyclohexyl chloride and bromide are somewhat lower than reported by Williams.[6] They are about 0.1 *D* higher than the corresponding *sec*-butyl halides indicating either a somewhat larger polarizability of the alicyclic group or, possibly, an appreciable atomic polarization in the cyclohexyl series. The moment found for *sec*-butyl chloride here agrees closely with that reported by Parts[7]: like the other secondary butyl halides it is about 0.12 *D* larger than the corresponding normal halide.

Experimental

Materials. Benzene.—Benzene was purified as previously described,[8] d^{25}_4 0.87355.

Allyl Bromide, Allyl Ethyl Ether, Allylamine, Benzylamine, *sec*-Butyl Chloride, Cyclohexyl Chloride and Cyclohexyl Bromide.—Commercial materials were dried and fractionated through an efficient packed column; $n^{25}D$ 1.4660, d^{25}_4 1.4201 (allyl bromide); $n^{25}D$ 1.3892, d^{25}_4 0.7596 (allyl ethyl ether); $n^{25}D$ 1.4225, d^{25}_4 0.7579 (allylamine); $n^{25}D$ 1.5407, d^{25}_4 0.9798 (benzylamine); $n^{25}D$ 1.3945, d^{25}_4 0.8666 (*sec*-butyl chloride); $n^{25}D$ 1.4600, d^{25}_4 0.9960 (cyclohexyl chloride); $n^{15}D$ 1.4956, d^{15}_4 1.3290 (cyclohexyl bromide).

Allyl Iodide.—Allyl bromide was refluxed with sodium iodide and the product was separated from the reaction mixture by fractionation; a second distillation, through an efficient packed column, was carried out in the dark; $n^{25}D$ 1.5482, d^{25}_4 1.7955. Dielectric constant and density measurements were carried out in the dark with freshly prepared material.

Allyl Cyanide.—Allyl cyanide was prepared from allyl bromide and potassium cyanide by the same technique used for the preparation of allyl iodide, but the product is not light sensitive, $n^{25}D$ 1.4039, d^{25}_4 0.8267.

***trans*-1-Bromopropene-1.**—This was separated from a mixture (Columbia Chemicals Co.) of the *cis* and *trans* isomers by repeated fractionation through an efficient packed column. The fraction of boiling point 62.8–63° (752 mm.) was used; $n^{25}D$ 1.4510, d^{25}_4 1.4048.

Bromoallene.—A sample of pure material prepared by the method of Jacobs and Brill[9] was the gift of Prof. T. L. Jacobs; $n^{25}D$ 1.5179.

Apparatus and Method.—Electric moments were determined in benzene solution at 25°; the apparatus and technique have been described.[8] The molar polarizations of the solutes at infinite dilution were derived from the measured dielectric constants and densities of six solutions, ranging from 0.0005 to 0.0025 in mole fraction of solute, by the method of Halverstadt and Kumler.[10] The constants *a*

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[3] N. B. Hannay and C. P. Smyth, THIS JOURNAL, **68**, 1005 (1946).

[4] W. H. King and H. A. Smith, *ibid.*, **72**, 3459 (1950).

[5] M. T. Rogers, *ibid.*, **69**, 1243 (1947).

[6] J. W. Williams, *ibid.*, **52**, 1831 (1930).

[7] A. Parts, *Z. physik. Chem.*, **B7**, 327 (1930).

[8] M. T. Rogers, THIS JOURNAL, **77**, 3681 (1955).

[9] T. L. Jacobs and W. F. Brill, *ibid.*, **75**, 1314 (1953).

[10] I. F. Halverstadt and W. D. Kumler, *ibid.*, **64**, 2988 (1942).

b, ϵ_1, v_1 and P_2 obtained for each compound are shown in Table I along with the observed molecular refractions and the electric moments. The significance of the symbols and the method of calculation are the same as used previously.[8] The probable error in the dipole moments is about ±0.10 D.

Acknowledgments.—The authors are indebted to Prof. T. L. Jacobs for the gift of a sample of bromoallene. The investigation of cyclohexyl bromide was carried out in collaboration with Prof. J. D. Roberts.

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Preparation of Pure, Dry Iodine

BY R. A. WASHINGTON AND S. N. NALDRETT

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It was suspected that some of the anomalous results observed in the kinetics of the exchange of iodine atoms between methyl iodide and free iodine are due to contamination by water, with the result that ionic exchange is made possible. To check the presence of water, iodine was recovered from an iodide solution to which radioactive water (T_2O) had been added. The iodine was then dried in a conventional manner by sublimation *in vacuo* over P_2O_5 and condensation in a trap cooled with Dry Ice–acetone or liquid air. The radioactivity of samples of iodine recovered in this manner corresponded to a water content of about 0.1%. A modification of the palladous chloride method[1] which is sometimes used for the estimation of iodine was devised, which leads to recovery of pure, dry iodine.

The procedure recommended is as follows: sulfite ion is removed from the required amount of 0.5 M NaI solution (containing radioactive iodine as required) by addition of $BaCl_2$ and removal of $BaSO_3$ by centrifuging. About 10% excess $PdCl_2 \cdot 2H_2O$ solution (10 g./liter N HCl) is added to a centrifuge tube containing the iodide solution, the tube is heated in a water-bath for 15 minutes, allowed to stand one hour, centrifuged, precipitate is washed free of Cl^- with water, washed with 95% EtOH and then with dry Et_2O. The centrifuge tube with the precipitate is then dried for one hour at 110° and sealed into a vacuum system free from mercury and grease.

The PdI_2 is apparently moisture-free at this stage, but can be heated to 250° in a vacuum of 10^{-6} mm. without loss of iodine. The PdI_2 is then heated to 350° (mercury boiling at 1 atm.) and the iodine is recovered in a tube cooled with liquid air. Using this procedure the discrepancy in the recovery of 10-mg. samples of iodine was ±1%. The iodine can also be recovered somewhat more quickly by heating the PdI_2 to 350° in a stream of hydrogen. Samples of iodine recovered from NaI dissolved in water with a tritium activity of 8.2×10^8 disintegrations/minute/gram had residual activities of 800 to 1800 d./min., indicating that the amount of water present had been reduced to the order of 10^{-6} g.

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[1] N. H. Furman, Editor, "Scott's Standard Methods of Chemical Analysis," D. Van Nostrand Co., Inc., New York, N. Y., 1939.