Thus

$$\lambda_m = C_0 \epsilon_m = \epsilon'_m (C_0 - \Delta C_0)$$
$$\lambda_d = C_0 \epsilon_d = \epsilon'_d (C_0 - \Delta C_0)$$

Therefore

$$\epsilon_m / \epsilon_d = \epsilon'_m / \epsilon'_d \tag{1}$$

where ϵ'_m and ϵ'_d are the molecular extinction coefficients in the simple aqueous solutions.

By virtue of the relation (1), one can determine $(C_0 - \Delta C_0)$, and the value of $\epsilon'_m((C_0 - \Delta C_0)/C_0)$ calculated therefrom must coincide with the experimental value of ϵ_m, if our model is correct.

The result of the comparison is very much satisfactory as seen in Table I.

Thus the above model may be said to be quantitatively confirmed.

INSTITUTE OF POLYTECHNICS, OSAKA CITY UNIVERSITY
OSAKA, JAPAN

Catalyzed Allylic Rearrangement of a 1,1,1-Trichloro-2-alkene to a 1,1,3-Trichloro-1-alkene

BY DONALD G. KUNDIGER AND HAROLD N. HANEY

RECEIVED AUGUST 31, 1953

1,1,1-Trichloro-2-methyl-2-propene (TMP) is rearranged to 1,1,3-trichloro-2-methyl-1-propene (allyl TMP) by the catalytic action of thionyl chloride. When a mixture of thionyl chloride and chloretone in 5 to 1 mole ratio was heated under reflux for 30 hours,[1] a ratio of 88% TMP to 12% allyl TMP was obtained; but when the thionyl chloride-chloretone mixture was heated for 48 hours, a ratio of approximately 50% TMP to 50% allyl TMP was found. By comparison, when pure TMP is heated at 100° for 48 hours, practically no rearrangement to allyl TMP occurs.[2]

The catalyzed allylic rearrangement of TMP is rationally explained by the following reaction path
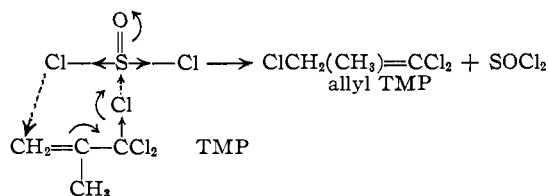
We have also found that TMP was rearranged to allyl TMP by powdered soft glass. The TMP (90%) underwent rearrangement in 12 hours at reflux. The electron donor character of the roughened and exposed inner surfaces of the alkaline glass powder may have been responsible for catalyzing this allylic rearrangement. The electron-donor character of the present catalyst is analogous in principle to that reported for ketene acetal where this acetal also catalyzed the present type of rearrangement.[2]

(1) We found it necessary to employ about 30 hours reaction of chloretone with purified thionyl chloride in order to obtain complete conversion of chloretone to TMP. Small amounts of allyl TMP are formed. Our experience thus differs from the work of S. M. McElvain and C. L. Stevens (THIS JOURNAL, **69**, 2669 (1947)) in which eight hours was mentioned as sufficient for 93% yield of TMP from chloretone.

(2) D. G. Kundiger and E. H. Froman, *ibid.*, **75**, 1744 (1953).

TMP was best separated from allyl TMP by flash distillation. In this manner an over-all accounting of 92% of the products of chloretone was obtained (81% TMP and 11% allyl TMP) with a reaction period of 30 hours.

Experimental Part

I. Reaction of Chloretone with Thionyl Chloride.— Purified chloretone (1.25 moles, 222 g.) and purified thionyl chloride (5.5 moles, 654.5 g.) were heated under anhydrous conditions and under reflux (about 79°) for 48 hours, while dry nitrogen gas was passed through to remove evolved hydrogen chloride and sulfur dioxide. *Anhydrous chloretone must be handled with special care and as rapidly as possible because of its extreme hygroscopicity.* The unreacted thionyl chloride was distilled off through a packed column under 140 mm. pressure. The residual liquid was transferred to a Claisen flask and distilled to give 150.9 g. (75.7%) of a 50–50 mixture of TMP and allyl TMP, b.p. 130–158° (the b.p. of TMP is 130–137°; the b.p. of allyl TMP is 152–158°). This mixture was preceded by a forerun of 7.5 g. which boiled largely at 125–130°. Note: Porcelain boiling chips prevented quite well the troublesome bumping and frothing always experienced with the distillation of the TMP–allyl TMP mixture. Use of a fairly large capillary ebulliator tube through which a slight stream of dry air is drawn with slight suction on the system is preferred. This product ratio was not changed by refluxing the 50–50 mixture for 3 hours or by refluxing in the presence of hydrogen chloride for 30 minutes.

Conversion of Chloretone to TMP.— The following experiment was designed to yield the maximum TMP isolable. The procedure was the same as the preceding experiment except that (a) the reaction mixture was held under reflux 30 hours (steam-bath), (b) half the amounts of the reactants were used, and (c) the crude product, after removal of thionyl chloride, was flash distilled (bath 197–202°). There were thus obtained (a) 80.8 g. (81%) of TMP, $n^{25}D$ 1.4831 (lit. 1.4853), b.p. 135–137°, and (b) residue, which when simply distilled gave 11.2 g. (11%) of allyl TMP, b.p. 153.5–157.2°, and undistilled residue, 3.7%.

Powdered Soft Glass as Catalyst in Allylic Rearrangement of TMP to Allyl TMP.— A teaspoonful of powdered soft glass was mixed into 193.5 g. of TMP in a 3-necked flask fitted with a reflux condenser, a sealed stirrer, and a thermometer in the liquid and protected from atmospheric moisture. Rapid mechanical stirring was necessary to prevent severe troublesome bumping during reflux. Effective stirring also kept the powdered glass suspended. With refluxing and external heating, the temperature in the liquid gradually rose to 157° at the end of 12 hours. Simple distillation of the liquid (crude allyl TMP) resulted in 3.1 g. of forerun, and 174.3 g. (90%) allyl TMP, b.p. 152–157°.

DEPARTMENT OF CHEMISTRY
KANSAS STATE COLLEGE
MANHATTAN, KANSAS

Chemistry of Aliphatic Phosphonic Acids. II. Dielectric Constants and Viscosity of Some Higher Alkylphosphonates

BY GENNADY M. KOSOLAPOFF

RECEIVED AUGUST 25, 1953

Several determinations of dipole moments of various trialkyl phosphates can be found in the chemical literature. However, only one set of such determinations in the class of alkylphosphonates exists; this set of values was obtained for a very restricted number of such esters.[1] As a part of a comprehensive study of these compounds we determined the dielectric constants of several diethyl alkylphosphonates, containing an even

(1) A. E. Arbuzov and P. I. Rakov, *Izvest. Akad. Nauk S.S.S.R., Otdel. khim., nauk,* **237** (1950).

TABLE I

RP(O)-(OEt)₂ R shown	B.p. °C.	Mm.	d^{32}_4	d^{62}_4	n^{32}D	η^{32}	η^{62} millipoises	ϵ^{31}	MR Found	Calcd.	μ, D
C₂H₅	86	14	1.0158		1.4108			10.653	40.56	40.77	2.95
n-C₇H₁₅	105	1.4	0.9525	0.9331	1.4242	33.26	21.45		63.25	63.86	
n-C₈H₁₇	114	1.1	.9401	.9228	1.4289	31.19	21.79	6.291	68.54	68.48	2.83
n-C₁₀H₂₁	144	1.8	.9293	.9124	1.4330	44.28	29.33	5.682	77.75	77.71	2.78
n-C₁₂H₂₅	174	3	.9206	.9041	1.4365	60.94	36.45	5.162	86.99	86.95	2.73
n-C₁₄H₂₉	180	1	.9144	.8988	1.4398	78.15	47.06	4.631	96.23	96.19	2.62
n-C₁₆H₃₃	177	0.4	.9098	.8944	1.4428	101.54	58.14	4.282	105.44	105.42	2.55
n-C₁₈H₃₇	189	0.4	.9041	.8890	1.4442	124.69	69.43	4.052	114.63	114.66	2.52

number of carbon atoms in the alkyl chain, and calculated their dipole moments.

In the course of this study we checked the applicability of the currently used value for the atomic refraction of the "phosphonate phosphorus." This value, 4.27, has been suggested by Kabachnik[2] some time ago. We found that this value applies excellently to the higher phosphonates.

The oily character of the higher alkylphosphonates suggests a possible interest in these esters as lubrication aids. For this reason we also determined the viscosities of these compounds at two temperatures. The viscosity–temperature relationship in this group of esters shows clearly a severe decline in viscosity at elevated temperatures. A minimum of the relative decline of viscosity was found for the compound with a ten-carbon alkyl chain. Since viscosity is a function of the molecular shape, this particular length of the phosphonate carbon chain is probably not necessarily the optimum one for the general class of dialkyl alkylphosphonates.

The dielectric constants of our esters were determined directly with the specimens, rather than with their solutions in non-polar solvents. The results shown in the Experimental Part indicate the downward trend of the dielectric constant with increase of the alkyl chain length. The calculation of the dipole moments from the dielectric constant values, as well as the measurements directly on the polar liquids, rather than on their solutions in solvents such as benzene, follow the reasoning given by Böttcher.[3]

As pointed out by Böttcher, the approximations employed in the derivation of his equation

$$\mu^2 = \frac{9kTM}{4\pi Nd} \times \frac{(\epsilon - n^2)(2\epsilon + n^2)}{\epsilon(n^2 + 2)^2}$$

tend to cancel, as shown by the results with numerous compounds. We employed the above equation in our calculation of the dipole moments of the phosphonates and the results are to be found in the Experimental Part. The calculation was carried out under the assumption that the Böttcher equation is valid for this group of compounds. Some justification for one of the assumptions implicit in this equation (namely, that of a point dipole in an essentially spherical molecule) appears to be found in the value of the dipole moment found by us, by this method, for diethyl ethylphosphonate.

(2) M. I. Kabachnik, Izvest. Akad. Nauk S.S.S.R., Otdel. khim, Nauk, 219 (1948).

(3) C. J. F. Böttcher, "Theory of Electric Polarisation," Elsevier Publishing Co., Amsterdam, 1952; specific reference is made to: pp. 186–187, 298, and 323–328. Also, see C. J. F. Böttcher, Physica, 6, 59 (1939); Rec. trav. chim., 62, 119 (1943).

Our value of 2.95 D is probably within the combined experimental errors of our work and that of Arbuzov and Rakov[3] who find the value of 2.91 D in dilute benzene solution. As a further check of this point, we determined the dielectric constant of this ester in dilute heptane solutions and calculated the dipole moment of the ester by the more conventional extrapolation of $P\infty$. In this instance the moment was found to be 2.84 D. This value is lower than that found by Arbuzov and Rakov for the same ester in benzene solution. This difference can be expected, however, in view of the "quasi-polar" nature of benzene as a solvent, with its relatively mobile electronic atmosphere, which is absent in a solvent like n-heptane.

The dipole moments, as calculated by us, show a distinct trend to lower values with an increase of the alkyl carbon chain. There is to be noted a definite decrease of this trend in the higher members, indicating a possible approximation to a limiting value. This trend may be a real one, or it can be an indication of incomplete validity of the Böttcher equation in the instance of the higher esters, caused by an elongated shape of the molecules.

While the information on the geometric disposition of the chains in esters of this type is not available, the data obtained through the parachor determinations indicate that compounds of this family tend to assume an "onion-shaped" structure about the central PO group with a form of a hydrogen bond linking the singular oxygen to the third atom from the phosphorus in all chains attached to the latter. This permits a compound like diethyl ethylphosphonate to assume a close approximation to the spherical molecule assumed in the derivation of the Böttcher equation. This type of bonding at the singular oxygen may be expected to bring the dipole moments of the entire series to a fairly narrow range of values. This range was found to be approximately 0.4 D in our series, from C₂ to C₁₈ members. In another series of determinations, currently in progress, we are examining a group of phosphorus derivatives in which the "onion-shaped" molecular structure cannot be attained.

Experimental Part

Preparation of the Esters.—The diethyl alkylphosphonates were prepared by heating triethyl phosphite with the various n-alkyl bromides, with continuous distillation of ethyl bromide.[4]

In an earlier paper[4] we reported difficulties in securing a satisfactory reaction by this method with the higher bromides and, for this reason, an argument was made in favor of the preparation of the higher phosphonates from dialkyl sodiophosphites. In the present work no such difficulty was encountered. A possible reason for the earlier difficulty

(4) G. M. Kosolapoff, This Journal, 67, 1180 (1945).

may lie in the presence of traces of nitrogenous bases in the phosphite used at that time.

The esters, whose constants are shown in Table I, were obtained in yields of 84% or better. The products were finally purified by distillation through a 15-plate ring-packed fractionating column.

Determination of Viscosity.—The determinations were made conventionally in an Ostwald viscosimeter at 32 and 52°, the results being correlated with water standard.

Determination of Dielectric Constants.—The determinations were made at 32° by means of the Sargent Oscillometer, Model V, which was calibrated with carefully purified substances, whose dielectric constants had been accurately established earlier.[5] The dielectric constants of the phosphonates fell within the substantially linear portion of the calibration curve of the instrument. Thus it was possible to determine the relative values of the dielectric constants of any two substances to four, or even five, significant figures from the readings of the instrument. However, the actual accuracy of the determinations was obviously limited by the accuracy of the values taken as standards, a situation that has been common in such determinations.

Calculation of the Dipole Moments.—The dipole moments were calculated by the Böttcher equation and the results are shown in Table I. The values of the dipole moments are estimated to be accurate within 0.02 D.

Acknowledgment.—We wish to acknowledge the financial aid of the Research Corporation in the form of a Frederick Gardner Cottrell grant for partial support of this work.

(5) E. Treiber, J. Schurz and H. Koren, *Monatsh.*, **82**, 32 (1951).

THE ROSS CHEMICAL LABORATORY
ALABAMA POLYTECHNIC INSTITUTE
AUBURN, ALABAMA

The Anisotropic Rate of Photographic Development of Single Crystals of Silver Chloride[1,2]

BY HENRY LEIDHEISER, JR., AND FRANCES H. COOK

RECEIVED SEPTEMBER 28, 1953

The purpose of this communication is to describe some preliminary experiments which show that the rate of photographic development of silver chloride is dependent upon the crystal face exposed at the surface.

Large single crystals of silver chloride[3] were machined in the form of spheres, 5/8" in diameter, with a small shaft for handling.[4] These spheres were etched to a depth of approximately 0.01" by agitating slowly in 1% sodium cyanide solution; X-ray photographs taken at grazing incidence and by back reflection indicated that the strains introduced by the machining operation were removed by

(2) When this manuscript was first submitted for publication, the reviewer suggested that we await the publication of the article by H. D. Keith and J. W. Mitchell, *Phil. Mag.*, **44**, 877 (1953), which describes a very extensive study of the formation of free silver on single crystals of silver bromide. Resubmission of this manuscript was postponed until copies of the article could be obtained. Of particular pertinence to the experiments reported herein is the statement by Keith and Mitchell: "Under comparable conditions, the surface density of reduction centers is usually greater on (111) than on (100) surfaces and the rate of reduction at individual centers appears higher."

(3) The crystal ingots were purchased from the Harshaw Chemical Co., Cleveland, Ohio. See H. C. Kremers, *J. Opt. Soc. Am.*, **37**, 337 (1947).

(4) See H. Leidheiser, Jr., and A. T. Gwathmey, *Trans. Electrochem. Soc.*, **91**, 97 (1947), for a description of the single crystal method of study.

this etching. Smooth and strain-free surfaces were obtained by rotating the crystal and lightly pressing against it a strip of wool flannel moistened with 1% sodium cyanide solution. The surfaces so obtained had the microscopic and macroscopic appearance of plate glass.

The polished crystal was washed thoroughly in water and allowed to dry. After additional exposure to artificial light at ordinary room lighting conditions, the crystal was immersed in a photographic developer such as Ansco Finex-L maintained at 5–7°. The crystal faces making small angles with the (111) plane rapidly became covered with minute grains of silver while the (100) face and the faces making small angles with the (100) plane remained free of silver for much longer periods of time. The (110) faces and surrounding area had an intermediate activity. The relative order of activity of the faces was the same in Eastman developers Dektol and DK-50. When a heavy deposit of silver was formed and the crystal was immersed in nitric acid, the silver was removed most rapidly from the (100) faces and surrounding areas.

X-Ray analysis at grazing incidence of the silver deposits indicated that on the same crystal the degree of preferred orientation of the deposit on the (100) face was greater than that of the deposit on the (111) face. The electron microscope observations made by Keith and Mitchell relative to the formation of filamentous silver in some cases and the formation of geometric figures in other cases were confirmed in this study.

It is not known at the present stage of progress whether the results reported herein represent differences in the rate of development of the latent image or simply differences in the fogging behavior of the crystal faces. An answer to this problem is being sought. Consideration will also be given in future studies to an analysis of the role of trace impurities such as silver oxide and silica on the results.

Additional experiments have indicated that the rate of etching of silver chloride crystals in acid fixing solution is also dependent on the crystal face exposed at the surface. Experimental work on the photographically important properties of silver chloride crystals is being continued.

VIRGINIA INSTITUTE FOR SCIENTIFIC RESEARCH
RICHMOND 20, VIRGINIA

Relationships between the Absorption Spectra of the 8-Quinolinol Chelates of the Group IIIb Metals and the Acidic Species of 8-Quinolinol

BY THERALD MOELLER AND FRED L. PUNDSACK

RECEIVED AUGUST 3, 1953

In the course of investigations of the 8-quinolinol and 5,7-dihalo-8-quinolinol chelates of the Group IIIb metals,[1,2] marked similarities between the absorption spectra of solutions of these compounds in "neutral" non-aqueous solvents and the spectra of acidic aqueous solutions of the reagents were noted.[2] Although the absorption spectra of acidic,

(1) T. Moeller and A. J. Cohen, THIS JOURNAL, **72**, 3546 (1950).

(2) F. L. Pundsack, Doctoral Dissertation, University of Illinois (1952).