[CONTRIBUTION FROM THE GATES AND CRELLIN LABORATORIES OF CHEMISTRY, CALIFORNIA INSTITUTE OF TECHNOLOGY, AND FROM THE GEORGE FISHER BAKER LABORATORY OF CHEMISTRY OF CORNELL UNIVERSITY]

The Alkyls of the Third Group Elements. II. The Electron Diffraction Study of Indium Trimethyl

BY LINUS PAULING AND A. W. LAUBENGAYER

In a previous paper[1] indium trimethyl has been shown to be monomeric in the vapor phase. Samples of the same preparation of this compound have been studied by electron diffraction methods.

The electron-diffraction photographs of indium trimethyl, prepared in the usual way with film distance 10.84 cm. and electron wave length 0.0613 Å., are rather poor, showing the strong background expected for a molecule containing such a heavy atom as indium. The pattern is approximately that of a single sin $1s/1s$ curve corresponding to an interatomic distance of about 2.1 Å., as expected for In–C; there is no indication at all of the important indium–indium terms which would occur for a dimer or other polymer.

Measured s_0 values for five maxima and four minima are given in Table I; two additional very faint maxima could also be seen, but not measured reliably. The sequence of s_0 values deviates somewhat from that for the In–C term alone, in the way corresponding to the effect of the In–H and C–C terms. In Fig. 1 there are shown theoretical scattering curves calculated for two models, A with the angle C–In–C equal to 109°28′ and B with this angle equal to 120°; for both models the values In–C = 2.21 Å., C–H = 1.09 Å., and angle H–C–In = 109°28′ were used. The H–H terms were neglected.

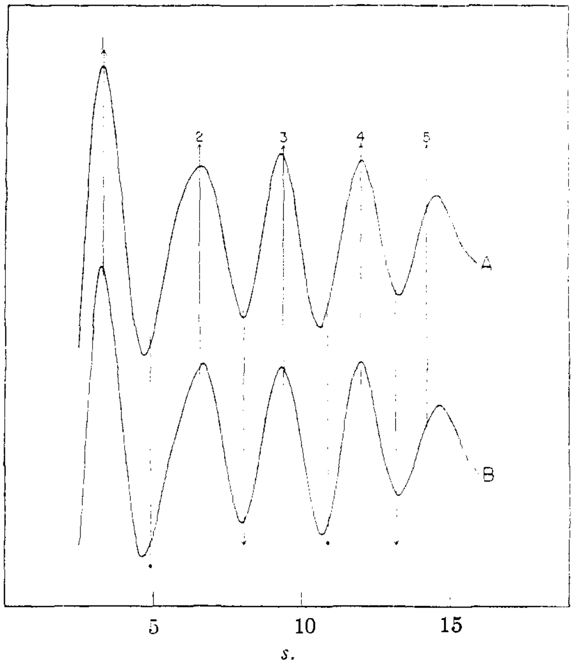

Fig. 1.—Simplified theoretical intensity curves for indium trimethyl, calculated with In–C = 2.21 Å., C–H = 1.09 Å., and angles H–C–In = 109°28′: A, angles C–In–C = 109°28′ (pyramidal model); B, angles C–In–C = 120° (planar model). The vertical lines represent the observed s_0 values multiplied by the factor 2.16/2.21.

TABLE I

ELECTRON DIFFRACTION PHOTOGRAPHS OF INDIUM TRIMETHYL

				Scaled.		In–C, Å.	
Max.	Min.	Intensity	s_0	Model A	Model B	Model A	Model B
1		10	3.38	3.30	3.26	2.16	2.13
	2		5.09	4.73	4.66	(2.06)	(2.02)
2		8	6.83	6.63	6.69	2.14	2.16
	3		8.28	8.10	8.00	2.16	2.14
3		6	9.63	9.33	9.33	2.14	2.14
	4		11.16	10.68	10.70	2.11	2.12
4		4	12.30	12.07	12.00	2.17	2.16
	5		13.51	13.35	13.29	2.18	2.17
5		2	14.60	14.60	14.70	2.21	2.22
					Average	2.16	2.16

The two curves are so similar in appearance that a decision between the models on the basis of the photographs cannot be made; it is of course probable that the second model is the correct one, since the indium atom is surrounded by only three pairs of valence electrons in this molecule, and would hence tend to form coplanar bonds. For each model the indium–carbon distance is found to be 2.16 Å., with an estimated probable error of 0.04 Å.

This indium–carbon bond distance is 0.05 Å. less than the sum of the tetrahedral radii of indium (1.44 Å.) and carbon (0.77 Å.). The decrease is expected in view of the presence of only a sextet of electrons about indium. The value In–C = 2.16 Å. corresponds to a trigonal radius of 1.39 Å. for the indium atom.

We are indebted to Dr. K. J. Palmer and Dr. V. Schomaker for assistance in the preparation and

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[1] Laubengayer and Gilliam, THIS JOURNAL, 63, 477 (1940).

measurement of the electron-diffraction photographs.

Summary

The In–C distance in indium trimethyl is found by the electron diffraction method to be 2.16 ± 0.04 Å.

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The Polyhydric Alcohol–Polybasic Acid Reaction. VI. The Glyceryl Adipate and Glyceryl Sebacate Polyesters

BY R. H. KIENLE AND F. E. PETKE

No quantitative data appear to have been published for the glyceryl adipate and the glyceryl sebacate polymerization reactions. In the present investigation, data are presented for the formation of these polyesters from glycerol and their respective acids. In addition, when considered jointly with the work published on glyceryl succinate,[1] the effect on the polyester formation reaction resulting from the increase in chain length of the dibasic acid is shown.

The apparatus and the technique used have been described previously.[2] The glycerol used was the same as that employed in all our recent polyester investigations. The adipic acid employed was chemically pure acid (du Pont) which was redistilled under 15 mm. presure, the fraction distilling between 222–224° being taken. The sebacic acid was Eastman Kodak Company purified product. Both polyester reactions were studied at 190°. This temperature was chosen in order that the data might be comparable with the previously published glyceryl succinate (acid) and glyceryl phthalate (acid) investigations.[3]

Experimental Data

The actual data obtained for the glycerol–adipic acid and glycerol–sebacic acid reactions are given in Figs. 1 and 2.

Figure 3 shows the acid value–water evolved relationship for both reactions. When the experimental curves for each polyester are compared with the theoretical curves, which assume that only interesterification occurs, it is found that the water evolved is at all times less than the theoretical. The deviation, however, is greater in the early portion of the reactions than near and at gelation. The acid value–water evolved relationships do not indicate anhydride formation as was found in the case of glyceryl phthalate. There is a suggestion that part of the water formed, especially in the early part of the reaction, is retained by the polyesters.

The log acid value–log time curves for the reactions are similar in shape to the corresponding plots for glyceryl phthalate (acid) and glyceryl succinate (acid). Changes of slope are observed in the curves around 50% esterification and at a degree of esterification corresponding to the formation of the monomer.

Analytical Data

Both of these polyesters were soft, stringy, flexible, very light colored resins. In the early stages they were balsam-like in character. At gelation both were rubbery. Large samples of each polyester very close to gelation were prepared and further examined in detail. The analytical data obtained on these samples are given in Table I.

TABLE I

		Glyceryl adipate	Glyceryl sebacate
Acid value		159.3	118.2
Saponification value		616.1	517.3
% esterification		74.0	77.1
Av. molecular weight		1260	1450
Ultimate analysis	C, %	52.6	60.3
	H, %	6.7	8.6

The infrared spectra from 1–15 μ for these resins have been measured[4] and are plotted in Fig. 4. The spectra show the necessary linkages for polyester formation. In addition, bands are observed around 14 μ which correspond to similar bands found in the free acids from which the polyesters were prepared. Bands such as these were missing in glyceryl succinate.

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[1] Kienle and Petke, THIS JOURNAL, **62**, 1053 (1940).

[2] Kienle, van der Meulen and Petke, *ibid.*, **61**, 2258 (1939).

[3] Kienle, van der Meulen and Petke, *ibid.*, **61**, 2268 (1939).

[4] Acknowledgment is made to Mr. R. R. Brattain for measuring these spectra.