-0.42 volt, and Latimer[10] has calculated it to be approximately -0.33 volt. According to Furman and Murray[5] the E_0 potential of the mercury–mercurous system in hydrochloric acid solution varies from about -0.4 volt in solutions of very low acidity to about 0.0 volt in solutions 9 N in this acid. These data account satisfactorily in a qualitative way for the experimental observations reported in the present paper. The E_0 potential of the uranous–uranyl system is so close to that of the mercury–mercurous system in solutions of very low acidity that only partial reduction to uranous ion can occur. With increase in concentration of acid the E_0 potential of the mercury-mercurous system finally rises so far above that of the uranous–uranyl system that reduction can become essentially complete. Moreover, by analogy with other corresponding systems it is very likely that the E_0 potentials of the uranous–uranyl system actually falls considerably with increasing acidity so that the difference between the E_0 potential of the two systems at high hydrochloric acid concentrations would be greater than the above data indicate. A rigorous treatment of the mutual relationships of the two systems considered here must await more precise measurements, particularly of the uranous–uranyl system.

Acknowledgments.—The experimental work reported in this paper was done by L. B. Rogers while holding a J. T. Baker Chemical Company Fellowship at Princeton University for the year 1941–1942. The authors thank Professor N. H. Furman and Dr. C. E. Bricker for helpful suggestions.

Summary

1. In solutions containing hydrochloric acid in sufficiently high concentration, uranyl ion is almost quantitatively reduced to uranous ion in the mercury reductor.

2. The simultaneous presence of both hydronium ion and chloride ion in high concentration is necessary. This may be explained from the E_0 potentials of the uranous–uranyl and the mercury–mercurous systems.

3. By the use of a small correction factor this reduction may be applied to the volumetric determination of uranium. The possible interference of uranium should be taken into account when using the mercury reductor for the determination of certain other elements.

PRINCETON, NEW JERSEY RECEIVED JUNE 10,1946

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(10) Latimer, "The Oxidation States of the Elements and their Potentials in Aqueous Solutions," Prentice-Hall, Inc., New York, N. Y., 1938, p. 239.

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF THE UNIVERSITY OF CALIFORNIA]

Electron Deficient Molecules. II. Aluminum Alkyls

BY KENNETH S. PITZER AND HERBERT S. GUTOWSKY[1]

In the first paper[1a] of this series, the most extensive series of electron deficient molecules, the boron hydrides, were considered and the concept of a protonated double bond advanced to account for their peculiar formulas. Aluminum trimethyl and triethyl[2] have also been reported to be anomalous in that they are dimeric under suitable conditions. We have prepared the methyl, ethyl, *n*-propyl, and *i*-propyl aluminum compounds and find all but the last to be dimeric under some conditions. Various data were obtained concerning these substances in the hope of elucidating the cause of their dimerization.

Experimental

Preparation of Compounds.—A very convenient method was developed for the preparation of aluminum trimethyl, based on the type of reaction described by Grosse and Mavity.[3] A distilling column of ten to twenty theoretical plate efficiency is fitted for use with an atmosphere of nitrogen either at 1 atm. or reduced pressure. Methyl iodide is placed with an excess of granular aluminum in the still pot and is mildly refluxed under 1 atm. of nitrogen for twelve or more hours until all methyl iodide has reacted. The temperature is then raised and the pressure reduced to about 10 cm. By maintaining a high reflux ratio, pure $Al_2(CH_3)_6$ may be taken off up to about 50% of the theoretical yield based on methyl groups. No doubt this yield could be increased by the use of greater fractionating power but this was not important for our purposes.

The initial reaction produces a general mixture of aluminum methyl iodides from which the most volatile, aluminum trimethyl, can be distilled. However, considerable fractionating power and a very slow take off are necessary so that the various rearrangement reactions may proceed. This preparation is far simpler for laboratory purposes than any previously used.

Unfortunately, the decreasing volatility of the higher alkyls prevented this new procedure from succeeding, even with the triethylaluminum. These compounds were prepared from the mercury alkyls.

Mercury ethyl, *n*-propyl and *i*-propyl were prepared without difficulty according to the method of Gilman and Brown[4]

$$2RMgX + Hg_2Cl_2 = HgR_2 + 2MgXCl$$

The mercury alkyls then reacted with aluminum in a bomb tube at 110° for about thirty hours. Aluminum ethyl and *n*-propyl were obtained in good yield. With the *i*-propyl compound a great deal of difficulty arose, presumably because of the instability of mercury *i*-propyl. In the only successful reaction the bomb tube was held at 60–70° for

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(1) Present address: Harvard University, Cambridge, Mass.

(1a) K. S. Pitzer, THIS JOURNAL, **67**, 1126 (1945).

(2) A. W. Laubengayer and W. F. Gilliam, *ibid.*, **63**, 477 (1941), who give references to earlier work. Professor Laubengayer in a private communication also states he has found these compounds to be dimeric in benzene solution.

(3) A. V. Grosse and J. M. Mavity, *J. Org. Chem.*, **5**, 106 (1940).

(4) H. Gilman and R. E. Brown, THIS JOURNAL, **52**, 3314 (1930).

twenty-four hours. By this time, the aluminum showed definite signs of amalgamation and the reaction was completed by heating for twenty-four hours additional at 110–120°.

Although the aluminum alkyls react somewhat with stopcock grease, it proved convenient to use stopcocks and ground glass joints in the general preparative work. However, the alkyls were finally vacuum distilled over aluminum in the absence of any grease into small glass ampoules which were then sealed off. The purity of preparations was checked by measuring the freezing point of the sample in each ampoule. In all cases, a series of samples was obtained whose freezing points agreed well within one degree, followed in some cases by less volatile fractions of lower freezing point. The latter were regarded as impure.

Negative mercury and halide tests were obtained on all samples used. Analysis of the aluminum triisopropyl gave 17.6% Al; theoretical value 17.3%.

Chemical and Physical Properties.—The alkyls are clear, water-white liquids at room temperature. The ethyl and *n*-propyl compounds are considerably more viscous than the methyl which resembles water. The *i*-propyl is intermediate. The four alkyls ignite spontaneously in air. Aluminum methyl and ethyl burn with a typical hydrocarbon flame, yellow and sooty. The aluminum *n*-propyl burns with a small pale blue flame. All react vigorously with water. The hydrolysis of benzene solutions after completing freezing point determinations gave this order of reactivity: methyl, *i*-propyl, ethyl, *n*-propyl.

Melting points were determined by shaking the ampoules to obtain a thin film of liquid on the upper part of the tube, freezing it in liquid air or an acetone–Dry Ice bath and obtaining the temperature above which the thin film of solid melted and below which it remained frozen. A pentane thermometer calibrated by the National Bureau of Standards was used for the melting points below 0°. The melting point of aluminum trimethyl has been reported as 15°[5] and aluminum triethyl only as less than −18°.[6]

TABLE I

MELTING POINTS AND DENSITIES

	$Al(CH_3)_3$	$Al(C_2H_5)_3$	$Al(n\text{-}C_3H_2)_3$	$Al(i\text{-}C_3H_7)_3$
M. p., °C.	15.0	−52.5	−107	2
d^{20}_4	0.752	0.837(?)	0.823	Not detd.

Densities were obtained by distilling the alkyls into calibrated pycnometers of 5 and 10 cc. volume, and applying a volume correction for the height of the liquid in the capillary. The high reactivity of aluminum trimethyl necessitated weighing the amount of grease applied to the ground glass joint on the pycnometer, sealing off the adapter and pycnometer as a unit, weighing it, and then the cleaned adapter. With the other alkyls, the pycnometer alone was removed, immediately cleaned of grease and stoppered by a clean weighed ground glass cap. No density determinations were found in the literature. The values in Table I are the result of at least two determinations. The samples of aluminum ethyl used for density determination were of somewhat questionable purity; the value in Table I may be too high.

The infrared absorption spectrum of aluminum trimethyl was determined by the spectroscopic department of the Shell Development Company, who report the absorption maxima in Table II. They state that the bands at 12.9 and 14–14.4μ are extremely intense, absorbing 100% even at about 2 mm. pressure.

The magnetic susceptibilities of aluminum trimethyl and triethyl were measured and the alkyls were found to be diamagnetic.

Solutions of aluminum trimethyl in benzene are essentially non-conducting. The specific conductivity of a solution of 0.18 mole of aluminum trimethyl per 1000 g. of benzene was determined to be approximately 1×10^{-7}.

TABLE II

WAVE LENGTHS, FREQUENCIES AND INTENSITIES OF INFRARED ABSORPTION MAXIMA OF ALUMINUM TRIMETHYL

Reported by the Spectroscopic Department of the Shell Development Co. 15-cm. cell, p = 12.6 mm.

λ(μ)	(cm.⁻¹)	Intensity
3.380	2958	7
3.425	2919	0[a]
3.49	2865	1[a]
3.735	2677	0 (?)
6.685	1496	0 (?)
6.925	1444	1[b]
7.67	1303	1
7.985	1252	7
8.295	1205	9
11.495	869	2
11.56	866	
12.875	779	10+
14.005	715	10+[b]
14.35	696	

[a] Indicates a shoulder. [b] A broad band.

The molar refraction of aluminum trimethyl has been computed to be 24.7 cc. (or 49.4 cc. for $Al_2(CH_3)_6$). This was obtained by combining the index of refraction, $n^{12}{}_D$ 1.432, as determined by Bleekrode[7] with a density of aluminum trimethyl, $d^{12}{}_4$ 0.758, calculated from $d^{20}{}_4$ 0.752, and $(\delta d/\delta t) = 0.00075$ g./cc. degree which were determined experimentally.

The ethyl, *n*-propyl, and *i*-propyl alkyls were observed to form viscous, high-boiling compounds when exposed to small amounts of oxygen. Residues of these materials were obtained after distillations and in two cases, preparations of aluminum *i*-propyl, the highly viscous material was obtained to the exclusion of any appreciable quantity of the desired compound. These products are possibly of the same kind as caused an irreversible increase in vapor density measurements of Laubengayer and Gilliam.[2] Although these compounds did not spontaneously ignite, they reacted vigorously with water. On exposure to air, they produced a pungent, heavy, sweet odor quite unlike that of the aluminum alkyls, which are more acrid. These materials gave higher values for both density and molecular weight than the alkyls from which they were derived. Possibly they contain aluminum–oxygen–aluminum links analogous to silicones.

Molecular Weight Measurements.—These were made in solution and for numerous reasons benzene was chosen as the solvent. A thiophene-free product was dried for several days over anhydrous magnesium perchlorate, then distilled from potassium in a 20 to 30 plate spiral gauze column at a reflux ratio of 10 to 1. The center fraction was recrystallized several times and about two-fifths rejected. The balance was stored over sodium–potassium liquid alloy and redistilled just prior to use; the first and terminal fractions were not used. The freezing points of the benzene used were between 5.325 and 5.335°.

The reactivity of the alkyls necessitated rigorous precautions in the formulation of a technique for determination of the freezing point lowerings. The cooling tube had a Beckmann thermometer and stirrer in the main chamber. A weighed ampoule of the alkyl and a silver-plated steel breaker were placed in a side arm and the assembled tube put on a high vacuum line and evacuated. The tube was left on the line for a minimum of two hours and until a vacuum of at least 3×10^{-5} was obtained. The tube was then filled with helium to one cm. above atmospheric pressure, the cap on the side arm removed and 25 cc. of the purified benzene pipetted in through a counter current of helium. The cap was replaced, the stopcock on the cooling tube was closed, and the tube removed from the vacuum

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(5) H. I. Schlesinger, R. T. Sanderson and A. B. Burg, THIS JOURNAL **62**, 3421 (1940).

(6) G. B. Buckton and W. Odling, *Ann. Spl.*, **4**, 109 (1865).

(7) M. L. Bleekrode, *Rec. trav. chim.*, **4**, 77 (1885).

line and placed in a cooling cell surrounded by an ice-bath. The cell was lined with asbestos paper to give a cooling rate of approximately 0.1°/min. at the freezing point of the solutions. The stirrer was manually operated for the last 2 to 4° of a run. Super-cooling was of the order of 0.1°; scraping of the stirrer along the side of the tube initiated crystal formation after which the temperature rapidly rose to a maximum and then remained substantially constant for at least a minute. This value, which was checked to 0.001° by warming the tube and recooling, was taken as the freezing point. After determining the freezing point of the benzene, the ampoule was broken, the solution thoroughly mixed, and its freezing point immediately determined. At the end of the run, the glass from the ampoule was collected and weighed in a sintered glass crucible, giving the weight of alkyl by difference.

The calorimetric heat of fusion of benzene[8] 30.09 cal./g. was taken as a more reliable basis of the freezing point constant than any of the direct measurements which scatter about the same value. Of the latter, the measurements of Peterson and Rodebush[9] with solutions of toluene in benzene agree very closely, whereas the more recent work of Batson and Kraus[10] with solutions of triphenylmethane in benzene differs by about one per cent.

Considering also the change of specific heat on fusion and assuming Raoult's law, one obtains

$$-\ln N_1 = 0.01523(T_0 - T)[1 + 0.0032\ (T_0 - T)]$$

which may be converted to the following working formula, accurate to second order terms

$$m_t = (T_0 - T)[0.1950 - 0.0021(T_0 - T)]$$

where m_t is the molality of the solute.

On this basis the values labelled m_t (Raoult) in Tables III to VI were obtained. The ratio of m_w, the number of moles of solute expressed as monomer, to m_t is the polymerization factor R. This would be 2 if all of the solute is dimeric and 1 if all monomeric.

There are two principal sources of uncertainty in these values. One is the deviation of the actual solutions from Raoult's law, which will be considered below. The other arises from possible reaction of the alkyl with impurities present. Indeed cruder techniques gave R values of 2.2 to 2.6 for aluminum trimethyl. In the final experiments only the slightest haze of aluminum oxide was observed when the ampoule of the methyl compound was broken and no evidence of reaction was noted for the higher alkyls. However, under these circumstances it is difficult to place limits of error on the results.

These results indicate clearly that aluminum trimethyl is essentially dimeric in agreement with the work of Laubengayer.[2] The ethyl and n-propyl are mostly dimer but with definite dissociation while the i-propyl compound is monomeric.

TABLE III

POLYMERIZATION FACTORS FOR ALUMINUM TRIMETHYL IN BENZENE SOLUTION

m_w	ΔT	m_t (Raoult)	R (Raoult)	m_t (cor.)	R (cor.)
0.6724	1.635°	0.3245	2.07	0.3367	1.997
.4808	1.181	.2332	2.06	.2395	2.008
.2483	0.620	.1217	2.04	.1234	2.012
.2382	.596	.1170	2.04	.1185	2.010
.1517	.380	.0744	2.04	.0750	2.023

TABLE IV

POLYMERIZATION FACTORS AND CONSTANTS FOR $Al(C_2H_5)_3$ IN BENZENE SOLUTION

$m_t(\text{cor.}) = m_t(\text{Raoult}) + 0.06\ m_w^2$

m_w	ΔT	m_t (Raoult)	R (Raoult)	m_t (cor.)	R (cor.)	K (cor.)
0.3453	0.877°	0.1726	2.00	0.1798	1.920	810
.2067	.539	.1057	1.95	.1083	1.908	990
.2013	.526	.1031	1.95	.1055	1.908	1010
.1906	.500	.0980	1.94	.1002	1.902	930
.1858	.487	.0955	1.94	.0976	1.904	1000
.1486	.395	.0773	1.92	.0786	1.891	960
.0972	.271	.0530	1.83	.0536	1.813	430
.0683	.192	.0375	1.82	.0378	1.807	570
					Av.	840

TABLE V

POLYMERIZATION FACTORS AND CONSTANTS FOR $Al(n\text{-}C_3H_7)_3$ IN BENZENE SOLUTION

$m_t(\text{cor.}) = m_t(\text{Raoult}) + 0.11\ m_w^2$

m_w	ΔT	m_t (Raoult)	R (Raoult)	m_t (cor.)	R (cor.)	K (cor.)
0.3145	0.839	0.1650	1.91	0.1759	1.788	100
.3018	.805	.1583	1.91	.1683	1.793	110
.1954	.531	.1041	1.88	.1083	1.804	193
.1796	.492	.0964	1.86	.0999	1.798	196
.1643	.452	.0885	1.86	.0915	1.796	209
.1144	.331	.0648	1.77	.0661	1.731	153
.1047	.302	.0591	1.77	.0602	1.739	180
.0835	.244	.0477	1.75	.0484	1.725	198
.0562	.169	.0330	1.70	.0333	1.688	212
.0422	.137	.0268	1.57	.0270	1.563	109
					Av.	166

TABLE VI

POLYMERIZATION FACTORS FOR $Al(i\text{-}C_3H_7)_3$ IN BENZENE SOLUTION

m_w	ΔT	m_t (Raoult)	R (Raoult)
0.2042	0.985°	0.1941	1.05
.1704[a]	.785	.1543	1.10[a]
.1498	.740	.1455	1.03
.0902[a]	.436	.0854	1.06[a]

[a] These data are known to be inaccurate. In the first case, the cooling tube was cracked when breaking the ampoule and, in the second, the benzene was impure. They are included merely as qualitative checks, since the difficulties in preparation of the aluminum i-propyl prohibited obtaining more extensive data.

Preparation and Freezing Point Lowering of a Mixed Methyl-i-propyl Alkyl.—From the preceding section it is seen that, whereas the methyl, ethyl and n-propyl alkyls of aluminum are

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[8] H. M. Huffman, G. S. Parks and A. C. Daniels, THIS JOURNAL, 52, 1547 (1930).

[9] J. M. Peterson and W. H. Rodebush, *J. Phys. Chem.*, 32, 709 (1928).

[10] F. M. Batson and C. A. Kraus, THIS JOURNAL, 56, 2017 (1934).

dimeric, the aluminum *i*-propyl is essentially a monomer. The large difference in properties between the *n*-propyl and *i*-propyl derivatives, while not unexpected, is still striking. The non-dimerization of the aluminum *i*-propyl could be explained by steric factors preventing Al–Al bonding or the non-availability of hydrogen atoms preventing bridge formation. In an effort to distinguish between these two possibilities, a mixed methyl-isopropyl alkyl was prepared and its polymerization determined.

Weighed ampoules of aluminum methyl and *i*-propyl, sealed under vaccum, were placed in a multi-armed glass cell. The cell was evacuated and sealed off. The ampoules were then broken and the alkyls distilled into a new ampoule by surrounding it with a liquid air-bath and heating the remainder of the cell. The ampoule was then sealed off and heated at a temperature of 110° for six hours, which may or may not have been necessary for the interchange of the alkyl groups. The freezing point lowering of the resulting alkyl was determined as previously described. The weight of the mixed alkyl was obtained as a check on the individual weights of the methyl and *i*-propyl alkyls. The results are given in Table VII.

TABLE VII

Weight $Al(CH_3)_3$	Weight $Al(i\text{-}C_3H_7)_3$	Weight Benzene	ΔT	
0.1779 g.	0.4168 g.	21.91 g.	0.591°	
$m_wAl(CH_3)_3$	$m_wAl(i\text{-}C_3H_7)_3$	Total m_w	m_t	R
0.1129	0.1218	0.2347	0.1160	2.02

At a concentration $m_w = 0.2347$, one may interpolate the values $R = 1.96$ for aluminum triethyl and $R = 2.04$ for aluminum trimethyl. Thus the polymerization factor for the mixed alkyl appears to be definitely higher than the ethyl compound even though it has more *i*-propyl groups than methyl groups and should consequently show more steric hindrance in an ethane-like structure. With the bridge structure the methyl groups can form the bridge leaving the isopropyl groups elsewhere.

Association Constants.—While the trimethylaluminum is completely dimeric and the *i*-propyl compound is monomeric, the ethyl and *n*-propyl show measurable dissociations. However, equilibrium constants calculated on the simple assumption of Raoult's law used above show marked variation with concentration. This is not unexpected since the aluminum alkyls need not have the same internal pressure as benzene. Considering first the aluminum trimethyl and following the methods of Hildebrand,[11] one obtains for $(\Delta E/V)^{1/2}$ for benzene 9.20 (cal./cc.)$^{1/2}$ from the energy of vaporization and density. For trimethylaluminum, one must estimate the change in heat of vaporization[2] with temperature, hence the value 7.4 is rather uncertain. However, from the freezing point data, assuming only dimeric molecules present, one may calculate a value 7.85 (cal./cc.)$^{1/2}$. Table III shows the corrected polymerization factor, R, on this basis. The slight increase of R (cor.) above two for the dilute solutions presumably arises from reaction with the solvent, which was never completely eliminated. Nevertheless, the consistency of the data is good and the internal pressure values agree as well as could be expected.[11]

Following the same procedure for the ethyl and *n*-propyl compounds, one seeks values of $(\Delta E/V)^{1/2}$ which will give constant values of the association constant K

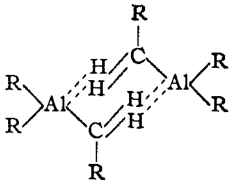
$$K = \frac{(Al_2R_6)}{(AlR_3)^2} = \frac{R - 1}{(2 - R)^2 m_t}$$

The resulting values of K are listed in Tables IV and V. The value of $(\Delta E/V)^{1/2}$ is 7.8 (cal./cc.)$^{1/2}$ for both aluminum ethyl and *n*-propyl. Furthermore, this is substantially the same internal pressure as was found for the aluminum methyl and is just a little larger than that for paraffin hydrocarbons[11] as might be expected. The variation in individual values of K is naturally fairly large, considering the possible errors in these data.

It seems hardly worth while to attempt to correct the data on the *i*-propylaluminum; however, it is apparent from Table VI that the deviations of R (Raoult) from one are of the same general magnitude as the corrections in the other cases. Hence, there is no evidence for any polymerization of this compound.

Discussion

From the results reported above, we can conclude first that the dimer is the one very definite polymer formed by certain aluminum alkyls—there is no substantial evidence for higher polymers.[12] In these compounds, one methyl group per aluminum suffices to form a very stable dimer. Two hydrogen atoms on the α carbon atom allow a dimer to form but of less stability.[13] Increasing the size of the group on the α-carbon from methyl to ethyl has little effect. No dimer is formed when only one hydrogen is left on the α carbon (two methyl groups having been substituted). These conclusions lead naturally to the following structure



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[11] J. H. Hildebrand, THIS JOURNAL, 57, 866 (1935); "Solubility," 2nd ed., Reinhold Publishing Co., New York, N. Y., 1936.

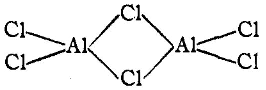
[12] L. M. Yeddanapalli and C. C. Schubert, *J. Chem. Phys.*, **14**, 1 (1946), suggested a tetramer but recently in a personal communication state that further experiments indicate only a dimer.

[13] A methyl group can form a bridge link in any of three rotational positions, while an ethyl or longer group must be rotated into the single correct position. With two such links a statistical factor of nine arises tending to dissociate the ethyl or larger compounds as compared to the methyl. This factor is almost enough to account by itself for the observed difference in stability.

While the binding of carbon through two hydrogens to aluminum suggests protonated double bonds such as were proposed for the boron hydrides,[1] it seems more likely that the polar character plays a predominant role. An aluminum atom carries considerable positive charge and attracts the negative, α carbon atom through and between the hydrogen atoms. The presence of more than one substituent essentially insulates the α carbon from the aluminum and the more distant carbon atoms are not sufficiently negative to form a significant bond. Of course the incompleteness of the valence shell of aluminum is important in exposing the positive charge of that atom.

Let us now see whether the physical properties of aluminum trimethyl support or are consistent with this structure. Skinner and Sutton[14] state that the electron diffraction pattern can be fitted with this type of structure together with several others.

The Raman spectrum offers the best support. Kohlrausch and Wagner[15] find that the number and general location of Raman lines in aluminum trimethyl is that expected from the series of aluminum halides which are known to have bridged structures. The more recent study of the halides by Bell and Longuet-Higgins[16] does not alter this conclusion. However, the polarization of the Raman lines indicates that the methyl compound has a lower symmetry than the chloride. Thus in the range below 700 cm.$^{-1}$ four polarized and five depolarized Raman active fundamentals are allowed for the symmetrical (D_{2h}) structure



For aluminum chloride there are three lines definitely polarized, three definitely depolarized, and two of doubtful polarization. This is good agreement with expectations. However, for aluminum trimethyl there are five lines definitely polarized and only one definitely depolarized with three doubtful.[17] Now the loss of symmetry of the structure here proposed for the methyl compound (as compared to the chloride) shifts two depolarized lines into the polarized group making six polarized and three depolarized. Furthermore, according to the Bell and Longuet-Higgins assignment, the two lines whose polarization should change are at 284 and 438 cm.$^{-1}$ in the chloride, and following the trends indicated by Kohlrausch and Wagner, these correspond to 314 and 563 cm.$^{-1}$ in the methyl compound. But the line at 284 cm.$^{-1}$ in the chloride is depolarized while that at 314 cm.$^{-1}$ in the methyl compound is definitely polarized. Both 438 and 563 are of doubtful polarization. Thus the Raman spectral data offer considerable support to the structure postulated for aluminum trimethyl.

From the infrared spectrum one can conclude little because it does not extend below about 700 cm.$^{-1}$. However, the lack of any marked deviations from the normal carbon–hydrogen stretching frequencies favors polar binding rather than protonated double bond character in the bridge. Also, the very high absorption coefficient for the aluminum–carbon bands near 700 cm.$^{-1}$ indicates a highly polar bond.

The high molar polarization found by Wiswall and Smyth[18] for aluminum trimethyl seems almost certainly to be due to large atomic polarization rather than a dipole moment. No likely structure gives a permanent dipole. The large atomic polarization is consistent with the high infra-red absorption intensities. The diamagnetic character and lack of color in aluminum methyl are consistent with this and other structures.

Having established that the structure proposed is consistent with the available data on the aluminum alkyls, we come to the problem of relating the properties of these compounds to those of other metal alkyls. If we were correct in concluding that the binding in the dimeric aluminum alkyls is largely polar, then the alkyls of all metals more electropositive than aluminum should also be associated. This appears to be true; however, the association[19] of second group alkyls proceeds further to the formation of relatively non-volatile solids. The third group metals whose alkyls have been studied, boron, gallium and indium, are all more electronegative than aluminum. Since aluminum alkyls are easily dissociated, it is not unreasonable that compounds of these other metals should be monomeric.[20]

Very recently Longuet-Higgins[21] has discussed the structure of aluminum trimethyl. While his proposals are generally similar to those of this paper, his detailed structures are not entirely compatible with the data and arguments presented here since one proposed a trimer and the other should allow a stable dimer with the isopropyl compound.

We wish to acknowledge with thanks the infrared spectrum of aluminum trimethyl obtained by the Spectroscopic Department of the Shell Development Company.

Summary

In order to study the nature of the binding in dimeric aluminum trialkyls, the methyl, ethyl, *n*-propyl and *i*-propyl compounds were prepared

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(14) H. A. Skinner and L. E. Sutton, *Nature*, **156**, 601 (1945).

(15) K. W. F. Kohlrausch and J. Wagner, *Z. physik. Chem.*, **B52**, 185 (1942).

(16) R. P. Bell and H. C. Longuet-Higgins, *Proc. Roy. Soc.* (London), **183**, 357 (1945).

(17) The value ρ = 0.66 is reported for the sum of the lines at 148 and 164 cm.$^{-1}$. Presumably one of these two must be polarized, while the other is probably but not necessarily depolarized.

(18) R. H. Wiswall, Jr., and C. P. Smyth, *J. Chem. Phys.*, **9**, 352 (1941).

(19) E. Krause and A. V. Grosse, "Die Chemie der metal-organischen Verbindungen," Verlag von Gebrüder Borntraeger, Berlin, 1937.

(20) Ref. 2, also Professor Laubengayer in a private communication states that he has found boron, gallium and indium alkyls to be monomeric in benzene solution.

(21) H. C. Longuet-Higgins, *J. Chem. Soc.*, 139 (1946).

and various properties measured. A new and more convenient preparation is reported for the methyl aluminum. The others were prepared from the mercury alkyls. Considerable difficulty was experienced with the *i*-propyl compound whose preparation has not been reported previously. The melting points, densities, and other properties were measured, together with the molecular weight in benzene solution (from freezing point measurements).

Aluminum trimethyl was found to be completely dimeric in the range studied while the ethyl and *n*-propyl compounds show measurable dissociation of the dimer. On the other hand, aluminum *i*-propyl is completely monomeric. Also, a mixed methyl-*i*-propyl compound was found to be more highly dimerized than the ethyl.

After making corrections for deviations from Raoult's law, association constants were calculated for the ethyl and *n*-propyl aluminum.

Consideration of these data together with the Raman spectrum and other published information leads to the conclusion that the binding is primarily a polar attraction of the positive aluminum atoms for the negative α carbon atoms This agrees with the fact that the alkyls of metals more electropositive than aluminum are all polymerized, usually into solids, while the alkyls of more electronegative metals are monomeric.

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The Heat Capacity, Heats of Fusion and Vaporization, Vapor Pressure, Entropy, Vibration Frequencies and Barrier to Internal Rotation of Styrene

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Styrene is one of the most important polymerizing monomers and its fundamental thermodynamic properties are, therefore, of considerable interest. A preliminary summary of these values has been published.[1] The directly measured data are presented in detail in this paper. The accompanying paper presents calculated values for the thermodynamic properties of the ideal gas at higher temperatures for styrene and for its methyl derivatives.

The potential barrier to the rotation of vinyl (*vs.* the phenyl) group is also of interest because of its relation to the energy associated with the conjugation of the vinyl and phenyl groups.

Apparatus.—The calorimeter and vapor pressure apparatus have been described previously.[2] The equipment used for *m*- and *p*-xylene was employed here without change.

Material.—An Eastman Kodak Company product was distilled through a 25-plate column, under reduced pressure, directly into the calorimeter. The boiling range was less than 0.1°. A few mg. of hydroquinone was added to prevent polymerization. Two samples were used in the measurements, the first of 76.099 g., or 0.7307 mole, the second of 78.189 g., or 0.7508 mole (based on vacuum weights, and a molecular weight of 104.144). From premelting measurements, the liquid-soluble, solid-insoluble impurity was estimated to be about 0.2 mole per cent.

Melting Point.—The equilibrium temperature at various fractions melted was observed, and plotted against the reciprocal of the fraction melted (Fig. 1). Extrapolation to infinite dilution gave the true melting point as 242.47 ± 0.05°K. Wood and Higgins[3] give the value −30.60° (242.56°K.).

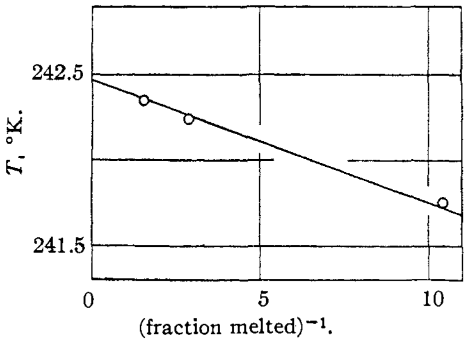

Fig. 1.—The melting point of styrene.

Heat Capacity.—The heat capacity of styrene was measured from 15° K. to room temperature, and the results, plotted in Fig. 2, are given in Table I. Values at rounded temperatures are given in Table II. The unit of energy is a defined calorie equal to 4.1833 Int. joules.

The heat capacity curve is unusual in that the solid has a larger heat capacity than the liquid at the melting point. The anomalous rise in the solid curve starts at about 140°K. which is 100° below the melting point. Presumably, it represents the beginning of a gradual or second order transition which is interrupted by the melting point. Similar behavior was observed in ethylene.[4] However, it is not obvious what the structural character of this transition might be

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[1] L. Guttman, E. F. Westrum, Jr., and K. S. Pitzer, THIS JOURNAL, **65**, 1246 (1943).

[2] K. S. Pitzer and D. W. Scott, *ibid.*, **65**, 803 (1943).

[3] L. A. Wood and C. F. Higgins, *India Rubber World*, **107**, 475 (1943).

[4] C. J. Egan and J. D. Kemp, THIS JOURNAL, **59**, 1264 (1937).