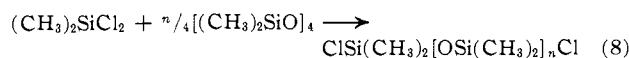


not consistently larger than the calculated values indicated that, except for  $R < ca. 0.3$ , there was less than 2–5% of the total Si in rings. For  $R = 0.192$ , there may be anywhere from 0 to 10% of the total Si in rings.

**Reorganization Kinetics in the Chloro System.**—The variation in the n.m.r. resonance peaks with time was measured on a mixture of dichlorodimethylsilane with octamethylcyclotetrasiloxane, proportioned so that equimolar amounts of silicon were derived from each species.

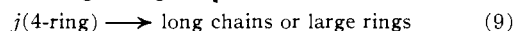


At 200° with 0.5 wt. % of  $\text{AlCl}_3$  as catalyst, it was found that the diminution of the *neso* molecules and of the total middle groups with time, as well as the increase of total end groups with time, gave a first-order plot over the period of time corresponding to the first half-life with a rather rapid switchover to a succeeding first-order plot for the remainder of the reaction (at least the next two half-lives). The half-life for the pseudo-first-order initial rate was found to equal 2.8 hr. and for the remainder of the process 7.8 hr. A similar experiment was carried out for a period of somewhat less than one half-life on the same mixture with no catalyst at the same temperature. In this case, first-order kinetics were again simulated and the measured half-life was 7560 hr. Even though there was undoubtedly a trace of  $\text{HCl}$  catalyst in the "uncatalyzed" system, it is seen that addition of only 0.5 wt. % of anhydrous aluminum chloride caused the reaction to go forty thousand times faster.

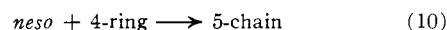
The variation of the change of the various measurable molecular species with time, as shown in Fig. 3, for this system at 200° with 0.5 wt. % aluminum chloride was calculated from the various resonance peaks as discussed in the previous section. Two prominent features of Fig. 3 are that the amount of tetra-rings decreases rapidly, the curves corresponding to the four- and five-membered chains go through broad maxima, and there is a sharp maximum for the middles in long chains or large rings as determined from n.m.r. peak  $M_6$  at

–0.067 p.p.m. A material balance, as well as subtraction of  $(M_3 + 2M_4)$  from  $E_3$ , shows that there are essentially no ends available for the middles in the long chains or large rings corresponding to  $M_6$  so that this curve in Fig. 3 truly corresponds to rings or macromolecular chains, including few if any chains shorter than the 20-membered molecule. By the way, it should be noted here that the resonance at –0.075 p.p.m. corresponding to tetrameric rings was reasonably well resolved from the one at –0.067 corresponding to middle groups not near the ends of chains so that, with good resolution, n.m.r. can be used to distinguish these two very similar types of middle groups.

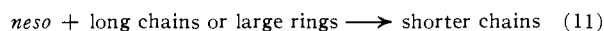
From the fact that the resonance corresponding to middle groups in long chains was the first to maximize, it is apparent that we have the following process occurring at the beginning of the reaction



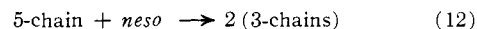
The early and prominent maximum noted for the five-membered chains shows that the following reaction is also initially prominent



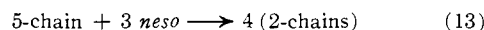
The rapid diminution in the long chains or large rings after they have maximized is most probably attributable to



Somewhat later on, it appears that the observed diminution of the five-membered chains is caused by the following mechanistically more complex over-all reactions



or, perhaps



After about 15 hr. under the experimental conditions of Fig. 3, it is apparent that all of the different species of molecules are in the process of exchanging parts with each other so that any theoretical explanation of the latter end of the curves of Fig. 3 must involve reactions between many different molecules, as must be the case at the final dynamic equilibrium.

[CONTRIBUTION FROM MONSANTO CHEMICAL CO., CENTRAL RESEARCH DEPARTMENT, ST. LOUIS, MO.]

## Exchange of Parts between Molecules at Equilibrium. II. Polyarsenous Oxyhalides

BY JOHN R. VAN WAZER, KURT MOEDRITZER, AND DAVID W. MATULA<sup>1</sup>

RECEIVED JULY 11, 1963

Dissolution of arsenous oxide in either arsenic trifluoride or trichloride gives homogeneous liquids, the viscosity of which increases greatly with increasing arsenous oxide content. Thus, for a liquid made by combining 5 moles of  $\text{AsX}_3$  with 6 moles of  $\text{As}_2\text{O}_3$ , the viscosity at 20° is about  $10^5$  poises as compared to a value near  $10^{-2}$  poise for the pure trihalide.  $F^{19}$  nuclear magnetic resonance (n.m.r.) shows that the oxide and fluoride react to give a nearly statistically random mixture of end, middle, and branch molecular structure building units, along with the equilibrium amount of the trifluoride molecule. These structure building units are combined together in various ways to form molecules based on As–O–As linkages, with each arsenic exhibiting an unshared pair of electrons. The fine structure in the n.m.r. spectra was interpreted in terms of the various arrangements of ends, middles, and/or branches around either an end or middle group. The coalescence of separate n.m.r. peaks as the temperature is raised, distillation at 0° of more  $\text{AsF}_3$  from a mixture than the amount originally present at equilibrium, and n.m.r. experiments based on mixing liquids exhibiting various proportions of  $\text{AsF}_3$  and  $\text{As}_2\text{O}_3$  show that structural reorganization in these molecules is very rapid even at 0°. For a composition made by combining 10 moles of  $\text{AsF}_3$  with 7 moles of  $\text{As}_2\text{O}_3$ , the average lifetime of the structure building units with respect to reorganization is *ca.* 0.5 sec. at 20° and *ca.*  $10^{-2}$  sec. at 100°, with an activation energy for the reorganization process of 9.5 kcal.

Although there appears to be no *a priori* reason that arsenic should not exhibit as rich and replete a chemistry as that of phosphorus, few arsenic-based families of

compounds have been described. A reasonable explanation for this may well be that the majority of arsenic compounds undergo structural reorganization so readily that classical methods of separation and identification are inapplicable. This paper is one of

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TABLE I

RELATIVE AREAS OF OBSERVED  $F^{19}$  N.M.R. PEAKS COMPARED TO CALCULATED PROPORTIONS OF TOTAL FLUORINE IN END OR MIDDLE GROUPS HAVING VARIOUS NEIGHBORING UNITS

| $R = F/As$        | Neso          |                       | End groups          |                         |             |                         |             |                         |                           |                         | Caled. from K $\Sigma e$ | 6.1 p.p.m. |                 |
|-------------------|---------------|-----------------------|---------------------|-------------------------|-------------|-------------------------|-------------|-------------------------|---------------------------|-------------------------|--------------------------|------------|-----------------|
|                   | Caled. from K | 0 p.p.m. <sup>a</sup> | 200[e] <sup>2</sup> |                         | 400[e][m]   |                         | 600[e][b]   |                         | 100[e] <sup>2</sup> [m]   |                         |                          |            |                 |
|                   | n             |                       | R(3-R) $ee$         | 3.1 p.p.m. <sup>a</sup> | R(3-R) $em$ | 4.4 p.p.m. <sup>a</sup> | R(3-R) $eb$ | 5.1 p.p.m. <sup>a</sup> | R(3-R) <sup>2</sup> $eme$ | 5.9 p.p.m. <sup>a</sup> |                          |            |                 |
| 3.00              | 100.00        | 100                   | 0.00                | 0                       | 0.00        | 0                       | 0.00        | 0                       | 0.00                      | 0                       | 0                        |            |                 |
| 2.74              | 83.39         | 81.1                  | 13.26               | 13.6                    | 2.50        | 3.8                     | .11         | 0                       | 0.52                      | 1.2                     |                          |            |                 |
| 2.53 <sup>b</sup> | 71.04         | 68.7                  | 18.92               | 19.7                    | 6.99        | 8.2                     | .60         | 0                       | 1.25                      | 2.1                     |                          |            |                 |
| 2.49              | 68.79         | 65.2                  | 19.58               | 20.9                    | 7.98        | 9.5                     | .79         | <0.5                    | 1.38                      | 2.7                     |                          |            |                 |
| 2.24              | 55.53         | 52.3                  | 21.31               | 21.2                    | 14.44       | 14.3                    | 2.28        | 3.7                     | 2.02                      | 3.2                     |                          |            |                 |
| 2.00 <sup>b</sup> | 44.10         | 44.0                  | 19.97               | 20.3                    | 20.04       | 20.2                    | 4.68        | <0.5                    | 2.24                      | 5.2                     |                          |            |                 |
| 2.00              | 44.10         | 43.8                  | 19.97               | 19.6                    | 20.04       | 19.2                    | 4.68        | 5.1                     | 2.24                      | 2.9                     |                          |            |                 |
| 1.74              | 33.16         | 33.9                  | 16.55               | 18.7                    | 24.19       | 23.4                    | 8.22        | 8.7                     | 2.04                      | 3.2                     |                          |            |                 |
| 1.49              | 24.09         | 24.4                  | 12.39               | 13.2                    | 25.51       | 24.9                    | 12.21       | 12.1                    | 1.58                      | 2.5                     |                          |            |                 |
| 1.25              | 16.76         | 15.5                  | 8.40                | 8.0                     | 24.07       | 23.8                    | 16.03       | 17.2                    | 1.04                      | 2.0                     |                          |            |                 |
| 0.98              | 10.13         | 10 <sup>c</sup>       |                     |                         |             |                         |             |                         |                           |                         |                          | 43.54      | 40 <sup>c</sup> |
| .89               | 8.30          | 11 <sup>c</sup>       |                     |                         |             |                         |             |                         |                           |                         |                          | 41.16      | 43 <sup>c</sup> |
| .87               | 7.92          | 5 <sup>c</sup>        |                     |                         |             |                         |             |                         |                           |                         |                          | 40.58      | 44 <sup>c</sup> |

<sup>a</sup> Chemical shift of the n.m.r. peak with respect to the *neso* compound,  $AsF_3$ . <sup>b</sup> Equilibrated at room temperatures. <sup>c</sup> Broad

several in this series that will be devoted to a study of various families of compounds based on arsenic. In these investigations, we are using experimental techniques which do not cause shifts in the reorganization equilibria, and especial attention is being given to the rates of reorganization.

The study reported here is primarily concerned with the system  $AsF_3-As_2O_3$ —a system which has not previously been investigated. However, it has been known for over a century<sup>2</sup> that arsenous oxide will dissolve in arsenic trichloride or tribromide. In the few papers<sup>2,3</sup> dealing with this subject, it is assumed that there is reaction between the oxide and halide, leading to the formation of oxyhalides; but none of these authors envisaged the full complexity of the system.

### Experimental Details

The arsenic trifluoride used in these studies was purchased from Chemical Procurement Laboratories, and the trichloride from the General Chemical Co. The arsenous oxide was a National Bureau of Standards standard sample for oxidimetry.

In a preliminary study, the dissolution of the arsenous oxide in the trihalide was carried out at room temperature in 15 mm. o.d. polyethylene test tubes. Under these conditions, complete dissolution could not be effected within 2 weeks for the over-all composition described by  $R = F/As < 2$ . For most of the data reported here, complete dissolution was achieved by heating the mixture overnight at 125° in 15 mm. thick-walled Pyrex tubes. For  $R = F/As < 1.25$ , there was still some undissolved  $As_2O_3$  after this treatment, but it all disappeared after an additional overnight heating at 200°. In all cases, the tubes were slowly rotated to give good agitation of their contents. Exploratory n.m.r. studies indicated that equilibrium between structure building units was achieved immediately upon dissolution of the oxide.

The  $F^{19}$  n.m.r. measurements were carried out with a Varian HR-60 spectrometer at a frequency of 56.444 Mc. Except that spinning was not used for n.m.r. determinations at elevated temperatures, all samples were spun in 5-mm. thin-walled precision-bore glass tubes; and chemical shifts are reported respectively to arsenic trifluoride, with positive shifts being upfield. In order to confirm the assignments, some additional referencing was carried out by adding small capillaries containing trifluoroacetic acid to the sample tubes. By this procedure, the shift of arsenic trifluoride with respect to trifluoroacetic acid was found to be  $-36.5$  p.p.m. The relative amounts of fluorine corresponding to the various n.m.r. peaks were measured by cutting out the peaks from a Xerox copy and weighing them.

Viscosity measurements on the more fluid samples were made with Ostwald-Fenske capillary viscometers and, on the more viscous ones, with a Haake rotational viscometer equipped with a plate-cone attachment. The viscometers were calibrated with standardized Newtonian oils obtained from the National Bureau of Standards. Some of the viscosity measurements at elevated

temperatures were subject to large error because of volatilization of  $AsF_3$  from the sample being studied and concomitant formation of crusts of  $As_2O_3$ . There was a similar problem at all temperatures because of partial hydrolysis of the samples to give HF plus  $As_2O_3$ . In spite of these difficulties with some of the samples, all of the compositions studied appeared to exhibit Newtonian flow with no time-dependent anomalies except for occasional irreproducible artifacts introduced by formation of an  $As_2O_3$  skin around the edge of the gap in the plate-cone viscometer.

After sitting for several weeks at room temperature, white crystals precipitated from the samples for which  $R < 1$ . X-Ray diffraction showed these crystals to be cubic arsenic trioxide, and careful inspection showed that there was none of this in the freshly prepared samples for which data are given below.

### Results and Interpretation

**Viscosity Data.**—The viscosities measured in the system  $AsF_3-As_2O_3$  are shown in Fig. 1, where the experimental points are compared with lines calculated from the equations

$$\log \eta = \alpha(1/T - \beta) \quad (1)$$

$$\log \alpha = 4.152 - 0.828R + 0.1140R^2 \quad (2)$$

$$\log \beta = -3.082 + 0.425R - 0.0358R^2 \quad (3)$$

where  $R$  is the  $F/As$  mole ratio giving the over-all composition in the system  $AsF_3-As_2O_3$ . Equations 2 and 3 were obtained from a curve-fitting routine involving the IBM-704 computer. These equations seem to represent the data adequately within experimental error, which for some compositions at certain temperatures was quite large.

It should be noted from Fig. 1 that the viscosity measurements cover a range of  $10^8$  poises, with the compositions corresponding to lower values of  $R$  exhibiting the higher viscosities and the greater temperature coefficients of viscosity. Since all samples were clear water-white, single-phase liquids, it seems reasonable to conclude that the high viscosities at low  $R$ -values ( $R = F/As$ ) are attributable to high molecular weights of the species making up these liquids. From a plot of the viscosity data at a given temperature *vs.* the  $R$ -value, it is seen that the viscosity rises very rapidly in the range from  $R = 1.5$  to 0.7, and this is true for any temperature from 0 to 100°. This indicates that the average size of the molecules must increase rapidly with decreasing  $R$  in this range which probably encompasses the "gel point"<sup>4</sup> of the system. On consideration of the common equation for viscosity,  $\eta = Be^{E_{vis}/RT}$ , we find from eq. 2 that the activation energy for viscous flow is given by the relationship

$$\log E_{vis} = 1.814 - 0.828R + 0.1140R^2 \quad (4)$$

(2) W. Wallace, *Phil. Mag.*, [4] **54**, 358 (1858); **55**, 261 (1859).(3) E. Thilo and P. Flögel, *Angew. Chem.*, **69**, 754 (1957).(4) W. H. Stockmayer, *J. Chem. Phys.*, **12**, 125 (1944); see eq. 6.

| 400[e][m] <sup>2</sup> |                     | 600[e][m][b]        |                     | 400[m] <sup>3</sup> |                     | Calcd. from K |                     | 1200[m] <sup>2</sup> [b] |        | 900[m][b] <sup>2</sup> |                     |
|------------------------|---------------------|---------------------|---------------------|---------------------|---------------------|---------------|---------------------|--------------------------|--------|------------------------|---------------------|
| R(3-R) <sup>2</sup>    | p.p.m. <sup>a</sup> | R(3-R) <sup>2</sup> | p.p.m. <sup>a</sup> | R(3-R) <sup>2</sup> | p.p.m. <sup>a</sup> | Σm            | p.p.m. <sup>a</sup> | R(3-R) <sup>2</sup>      | p.p.m. | R(3-R) <sup>2</sup>    | p.p.m. <sup>a</sup> |
| <i>emm</i>             |                     | <i>emb</i>          |                     | <i>mmm</i>          |                     |               |                     | <i>mmb</i>               |        | <i>bmb</i>             |                     |
| 0.00                   | 0                   | 0.00                | 0                   | 0.00                | 0                   |               |                     | 0.00                     | 0      | 0.00                   | 0                   |
| .20                    | <0.5                | .01                 | 0                   | 0.02                | 0                   |               |                     | .00                      | 0      | .00                    | 0                   |
| .92                    | 1.3                 | .08                 | 0                   | .17                 | 0                   |               |                     | .03                      | 0      | .00                    | 0                   |
| 1.13                   | 1.7                 | .11                 | <0.5                | .23                 | 0                   |               |                     | .04                      | 0      | .00                    | 0                   |
| 2.74                   | 3.4                 | .43                 | 1.9                 | .93                 | <0.5                |               |                     | .29                      | <0.5   | .02                    | 0                   |
| 4.49                   | 2.7                 | 1.05                | 4.7                 | 2.25                | <0.5                |               |                     | 1.05                     | 2.9    | .12                    | 0                   |
| 5.98                   | 5.1                 | 2.03                | 3.2                 | 4.37                | 1.1                 |               |                     | 2.97                     | <0.5   | .12                    | <0.5                |
| 5.98                   | 5.3                 | 2.03                | 5.1                 | 4.37                | 1.7                 |               |                     | 2.97                     | <0.5   | .50                    | <0.5                |
| 6.49                   | 6.0                 | 3.11                | 5.0                 | 6.68                | 8.0                 |               |                     | 6.40                     | 3.2    | 1.53                   | 0.7                 |
| 5.97                   | 8.7                 | 3.98                | 4.5                 | 8.55                | 6.9                 |               |                     | 11.40                    | 11.5   | 3.80                   | 1.9                 |
|                        |                     |                     |                     |                     |                     | 46.33         | 50 <sup>c</sup>     |                          |        |                        |                     |
|                        |                     |                     |                     |                     |                     | 50.54         | 46 <sup>c</sup>     |                          |        |                        |                     |
|                        |                     |                     |                     |                     |                     | 51.60         | 51 <sup>c</sup>     |                          |        |                        |                     |

flat peaks.

Viscosity measurements on the system AsCl<sub>3</sub>-As<sub>2</sub>O<sub>3</sub> led to results similar to those found for the AsF<sub>3</sub>-As<sub>2</sub>O<sub>3</sub> system. These findings are not reported in detail here, since they were based only on a few determinations plus visual inspection.

**Interpretation of F<sup>19</sup> Resonances.**—In the system AsF<sub>3</sub>-As<sub>2</sub>O<sub>3</sub>, thirteen F<sup>19</sup> n.m.r. peaks were found to appear at two or more R-values. A small one of these, at +10.0 p.p.m. from the AsF<sub>3</sub> reference, was attributable to an impurity present in the arsenic tri-fluoride since it was seen in the starting material (R = 3.00) and made up ca. 1% of the total fluorine in all compositions. The areas of the remaining resonance peaks as normalized on the basis of the total F are presented in the alternate columns of Table I. In interpreting the data of this table, we assume, on the basis of our previous experience,<sup>5,6</sup> that the system consists of molecules made up solely from the structure building units

AsF<sub>3</sub>    AsF<sub>2</sub>(O<sub>1/2</sub><sup>-</sup>)    AsF(O<sub>1/2</sub><sup>-</sup>)<sub>2</sub>    As(O<sub>1/2</sub><sup>-</sup>)<sub>3</sub> (5)  
 meso molecule, *n* end group, *e* middle group, *m* branch group, *b*

where O<sub>1/2</sub><sup>-</sup> stands for half of a bridging oxygen. In the system at equilibrium, the exchange of bridging oxygens for fluorine atoms is described by the equilibrium constants given as eq. 6 and 7

$$K_1 = [m][n]/[e]^2 \quad (6)$$

$$K_2 = [b][e]/[m]^2 \quad (7)$$

Excluding the meso compound which corresponds to the resonance at 0 p.p.m., there is a problem of assigning the eleven remaining peaks in Table I. These peaks must be attributable only to end and middle groups having various placements in the molecules,<sup>6</sup> since the branch group contains no fluorine. Furthermore, it does not appear that any of the important resonance peaks shown in Table I are components of spin-spin multiplets. This conclusion is in accord with the small amount of coupling<sup>7</sup> generally observed between fluorine atoms separated by several intermediate atoms and the relatively large quadrupole moment of the arsenic (As<sup>75</sup>, 100% natural abundance).

Two of the eleven remaining peaks are broad ones seen only at R < 1 when the other peaks have dis-

(5) L. C. D. Groenweghe, J. H. Payne, and J. R. Van Wazer, *J. Am. Chem. Soc.*, **82**, 5305 (1960); and E. Schwarzmann and J. R. Van Wazer, *ibid.*, **82**, 6009 (1960).

(6) K. Moedritzer and J. R. Van Wazer, *ibid.*, **86**, 802 (1964).

(7) N. Muller, P. C. Lauterbur, and G. F. Svatos, *ibid.*, **79**, 1807 (1957).

appeared. These two broad peaks are obviously the summation of a number of the peaks appearing at R values > 1. The remaining nine peaks are probably due to a first-order environment of end and middle groups, since this requires three kinds of end groups

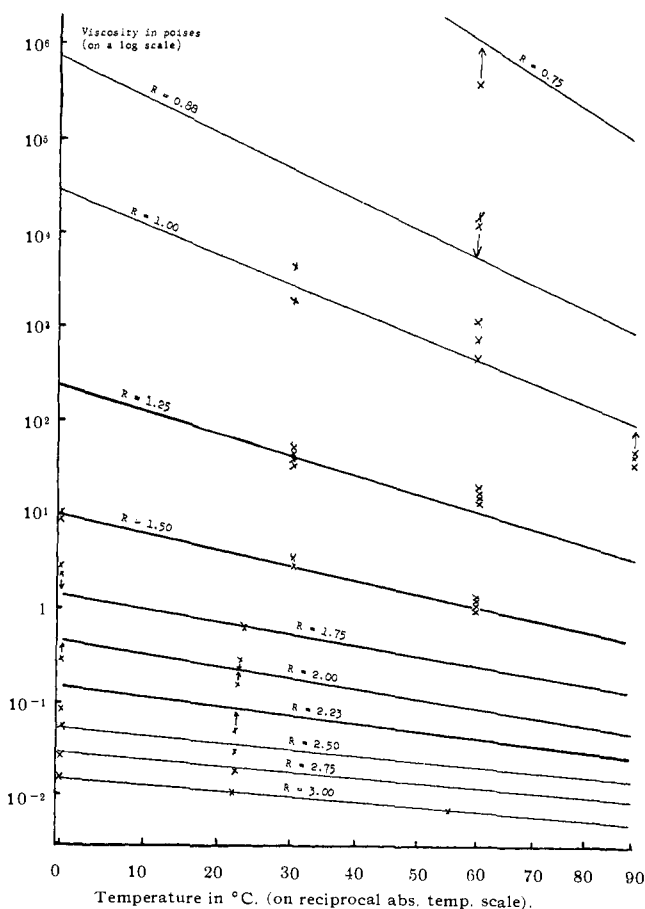


Fig. 1.—Viscosity of various compositions in the system AsF<sub>3</sub>-As<sub>2</sub>O<sub>3</sub> as a function of temperature.

(*ee*, *em*, and *eb*) and six kinds of middle groups (*eme*, *emm*, *emb*, *mmm*, *mmb*, and *bmb*). From inspection of the data of Table I, it seems logical to assign the resonance at 3.1 p.p.m. to the two ends in the di-chain and the resonance at 5.9 p.p.m. to the middle group in the tri-chain. The two peaks at 4.4 and 5.1 p.p.m. lying between these two tentatively

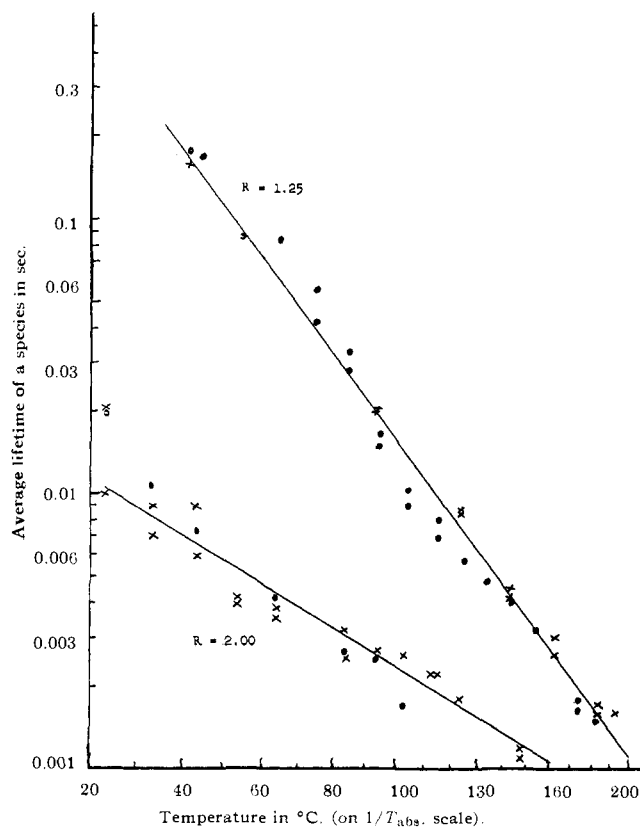


Fig. 2.—Variation of the life of the structure building units with respect to exchange of parts as a function of reciprocal absolute temperature. The slope of the line for  $R = 1.25$  corresponds to an activation energy of 9.5 kcal., and the slope for  $R = 2.00$  to 4.3 kcal. The circles represent data from n.m.r. peak broadening, assuming  $w_0$  is 11 c.p.s. (eq. 8) and the crosses are from peak coalescence (eq. 9).

assigned are then reasonably attributed to the end group attached to a middle group and the end attached to a branch, respectively.

From the assignment of the resonances at 3.1, 4.4, and 5.1 to end groups, we obtain the amount of *neso*, ends, middles, and branches. We further assume that, for values of  $R < 1$ , the viscosity-broadened n.m.r. peak at 6.1 p.p.m. corresponds to all kinds of ends and that at 9.1 to all of the middles. Statistical treatment of these data leads to the following values of the equilibrium constants of eq. 6 and 7:  $K_1 = 0.33$  with a standard deviation of 0.06, and  $K_2 = 0.31$  with a standard deviation of 0.02.

The six resonances corresponding to middle groups for  $R > 1$  were readily assigned in Table I where the percentage of the total number of monofunctional substituents (fluorine atoms) present as ends or middles having the stated first-order environment were calculated from the random probability of the sorting of parts into molecules.<sup>8</sup> A number of other distributions of the eleven peaks into the end and middle categories was tested on an empirical basis, ignoring the concept of order of environment introduced in paper I. However, none of these alternative assignments gave as little statistical error in the calculation of the equilibrium constants of eq. 6 and 7 as did the assignment used in Table I. Furthermore, the individual resonances could not be reasonably attributed to sensible arrangements of the atoms in the molecules using the alternative assignments. We therefore conclude that the assignments of Table I are correct.

(8) The particular equations shown in Table I were derived from the same statistical theory used by W. H. Stockmayer, *J. Chem. Phys.*, **11**, 45 (1943), and ref. 4, and by P. J. Flory, *J. Am. Chem. Soc.*, **74**, 2718 (1952).

The generally good agreement in Table I between the experimental data and the theoretical values calculated on the basis of random sorting of structure building units with rings disallowed indicates that there are not large amounts of ring compounds in this system. Indeed, the arsenous oxyfluorides are seen to approach ideal randomness not only with respect to the sorting of building units into molecules but also with respect to the sorting of substituents between building units so as to change their functionality (since for ideal randomness  $K_1 = K_2 = 0.333$  in such systems).

**Rates of Reorganization.**—The composition for which  $R = 2.00$  was vacuum distilled at 2 mm. pressure and  $0^\circ$  to remove the arsenic trifluoride. In 27 hr., 55% of the  $\text{AsF}_3$  originally used in making up this composition was distilled (as the pure form, by n.m.r.) from the sample which had only 44% of the original  $\text{AsF}_3$  present as such in the equilibrium mixture according to the n.m.r. data (see Table I) prior to distillation. This means that, even at  $0^\circ$ , the rate of reorganization was rapid with respect to the rate of distillation. The rate of distillation was found to diminish greatly when the viscosity approached a value in the neighborhood of 10 poises.

Another preliminary study to determine the rate of reorganization was carried out by adding 8.41 moles of arsenic trifluoride to 9.08 moles of the composition for which  $R = 2.00$ . Although the n.m.r. trace was completed within 4.5 min. after mixing, it was found, within experimental error, to be the same as that measured for an  $R$ -value of 2.49 at equilibrium. The amount of added arsenic trifluoride changed the overall  $R$ -value of the composition from 2.00 to 2.49. This means that reorganization equilibrium is achieved within 4.5 min. at  $25^\circ$ .

**Rates from  $\text{F}^{19}$  N.m.r. at Elevated Temperatures.**—For  $R = \text{F}/\text{As}$  values from 1.25 to 3, it was found that high-temperature n.m.r. measurements showed peak broadening and, at the higher temperatures, coalescence of the peaks. Finally the eleven peaks distinguishable at room temperature are reduced to three broad resonances at  $194^\circ$ . For  $R$ -values below 1, the three broad peaks present at room temperature were found to sharpen as the temperature was raised and then to broaden at the higher temperatures. This is a case of the two counteracting effects of reducing the viscosity broadening (see Fig. 1) and introducing exchange broadening as the temperature increases.

Two cases of exchange broadening were carefully studied. These corresponded to  $R = 1.25$  and  $R = 2.00$ . By use of eq. 8, for  $R = 1.25$ , we were able to obtain the average lifetime of the *neso* and the two prominent end species (corresponding to resonances at 3.1 and 4.4 p.p.m.) from the broadening of the peaks<sup>9</sup> (in the temperature range from  $50$  to  $100^\circ$  for the end-group resonances, and from  $50$  to  $150^\circ$  for the *neso* resonances).

$$1/\tau = 2\pi(w - w_0) \quad (8)$$

where  $w$  is the width of the resonance peak in c.p.s. at half height and  $w_0$  is a similar measure on the peak at the same sweep rate when the exchange is sufficiently slow as to not cause line broadening;  $\tau$  is the average life in sec.

When eq. 8, corresponding to slow exchange, was no longer applicable because of coalescence of the peaks, we were able to use eq. 9, which, though only theoretically valid<sup>9</sup> for a single pair of peaks, gave results

(9) J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High-Resolution Nuclear Magnetic Resonance," McGraw-Hill Book Co., Inc., New York, N. Y., 1959, pp. 220-225. See Fig. 10-1 on p. 223 for the values of  $A$  in eq. 9 of this paper.

equivalent to those obtained from eq. 8

$$\tau = A/2\pi(\nu_1 - \nu_2) \quad (9)$$

where  $A$  is a constant<sup>9</sup> ranging from 0.5 to 10, and  $\nu_1$  and  $\nu_2$  are the frequencies in c.p.s. of the neighboring lines. It was assumed that  $A = \sqrt{2}$  when the saddle between a neighboring pair of peaks barely disappeared. The data obtained by use of eq. 8 and 9 are reported in Fig. 2. We found that treatment of any of the single resonances by eq. 8 or pairs of neighboring resonances by eq. 9 gave data which fitted on a single line for a given composition in the  $\text{AsF}_3\text{-As}_2\text{O}_3$  system. Thus, within better than an order of magnitude, the rates of exchange between the various structural units are the same. This exchange may involve fluorine for fluorine and/or fluorine for bridging oxygen. However, exchange of oxygen solely for oxygen cannot lead to the observed n.m.r. spectra since the *meso* peak would not broaden with this kind of exchange but instead there would simply be coalescence of the end peaks with each other and the middle peaks with each other.

### Discussion

The gel point has been calculated to occur at  $R = 1.485$  assuming that the macromolecules do not contain small rings. This  $R$ -value is probably near the true gel point since an appreciable tendency for the formation of small rings would give unduly high values in Table I for the n.m.r. resonance peak at 8.6 p.p.m. (especially for  $R$ -values  $\geq ca.$  1.5, there should be some simple molecules based on small rings). Since flow is found for  $R$ -values considerably smaller than 1.485, it would appear that the flow process—at least in the more viscous systems—involves the making and breaking of As-O-As linkages.

It is interesting to note that for  $R = 2.0$ , the activation energy for viscous flow calculated from eq. 4 is 4.11 kcal. as compared to the approximate value of 4.3 kcal. for the activation energy for the fluorine exchange measured by n.m.r. (see Fig. 2). Likewise, for the composition corresponding to  $R = 1.25$ , the activation energy for flow is 9.06 kcal. as compared to 9.5 kcal. for the fluorine exchange. These results probably mean that the energy barrier for flow is the same as that for the observed exchange involving fluorine atoms.

The  $\text{AsF}_3\text{-As}_2\text{O}_3$  system studied here represents an interesting intermediate case where the rate of reorganization is so fast that one could not hope to separate individual species at room temperature. However, these species have a reasonably long lifetime and there is no question as to their existence. This system is roughly halfway between the very stable molecules based on C-C linkages and the extremely rapidly reorganizing association polymers linked together by hydrogen bonds; e.g., water and glycerol.

Since the equilibrium constants for reorganization in the  $\text{AsF}_3\text{-As}_2\text{O}_3$  system are close to random, this means that a number of the smaller branched molecules will be present in relatively large amounts in equilibrium with the other species for  $R$ -values in the neighborhood of 1.5–2.0. Thus, the "isotetra" molecule based on three ends and one branch is calculated<sup>4</sup> to be present to the amount of 1.1% and the "isopenta" molecule based on three ends, a middle, and a branch to correspond to 1.4% of the total arsenic in the mixture of polyarsenous oxyfluoride molecules with an  $R$ -value of 1.74.

**Acknowledgment.**—We wish to thank Claude H. Dungan for running the many  $\text{F}^{19}$  n.m.r. spectra involved in this study and Allan W. Dickinson for the necessary computer runs.

[CONTRIBUTION FROM MONSANTO CHEMICAL CO., CENTRAL RESEARCH DEPARTMENT, ST. LOUIS, MO.]

## Exchange of Parts between Molecules at Equilibrium. III. Nonrandom Redistribution of Dialkylamino Groups and Halogens on Triply Connected Phosphorus

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RECEIVED JULY 11, 1963

Ligand-interchange reactions were carried out between  $\text{PCl}_3$  and  $\text{P}[\text{N}(\text{C}_2\text{H}_5)_2]_3$ ,  $\text{PCl}_3$  and  $\text{PCl}[\text{N}(\text{CH}_3)_2]_2$ ,  $\text{CH}_3\text{PCl}_2$  and  $\text{CH}_3\text{P}[\text{N}(\text{CH}_3)_2]_2$  or  $\text{CH}_3\text{P}[\text{N}(\text{C}_2\text{H}_5)_2]_2$ ,  $\text{CH}_3\text{PBr}_2$  and  $\text{CH}_3\text{P}[\text{N}(\text{CH}_3)_2]_2$ ,  $\text{CH}_3\text{P}[\text{N}(\text{C}_2\text{H}_5)_2]_2$  and  $\text{PCl}_3$ , and between  $\text{CH}_3\text{PCl}_2$  and  $\text{P}[\text{N}(\text{C}_2\text{H}_5)_2]_3$ . In all cases, the equilibrium constant for disproportionation of the intermediate compounds obtained by exchanging halogens and dialkylamino groups was found to be so small that it could not be detected within experimental error ( $K < 5 \times 10^{-4}$ ) from the stoichiometry of the reaction products. However, from calorimetric measurements of the enthalpy of the disproportionation reaction, the equilibrium constants were calculated on the assumption that the entropy consists only of the entropy of mixing. The heat of formation of bis-(diethylamino)-chlorophosphine was found to be  $-76$  kcal./mole and of diethylaminodichlorophosphine  $-77$  kcal./mole. The exchange of chlorine and dialkylamino groups between triply connected phosphorus atoms represents the unusual case corresponding to a large enthalpy for a redistribution reaction.

### Introduction

Although this series is primarily concerned with the elucidation of families of compounds, a few papers will be devoted to the scrambling reactions of *meso* molecules when such studies give important information concerning exchange of parts between molecules. In this paper such work is reported.

In single-phase equilibrium reactions in which two or more different types of substituents undergo exchange between a given kind of central atom or moiety, there is no bond-energy contribution to the free energy of the exchange reactions since the total number of

bonds between the various pairs of bonded atoms remains constant. Thus, to the same approximation that constant bond energies,<sup>2</sup> electronegativities, and, where appropriate, *a priori* assignments of  $\pi$ -bond contributions to the enthalpy<sup>3</sup> may be used to calculate the heat of a reaction, it is expected that the enthalpy of a scrambling reaction will be zero. This paper presents information concerning a system in which there is a large enthalpy contribution to the free energy which causes the scrambling equilibria to be extremely nonrandom. Although a considerable amount of information is available on reorganization of substit-

(2) E.g., M. L. Huggins, *J. Am. Chem. Soc.*, **75**, 4123 (1953).

(3) J. R. Van Wazer, "Phosphorus and Its Compounds," Vol. I, Interscience Publishers, Inc., New York, N. Y., 1958, pp. 28–34; also Chapter 12.

(1) On leave of absence during 1960 from Monsanto Research S. A., Zurich.