These observations and comparisons suggest that the base hydrolyses of the chloropentaamminechromium(III) and chloropentaamminecobalt(III) complexes do not proceed through a common mechanism. It seems likely that the chromium complex hydrolyzes *via* a mechanism which involves direct interaction and charge transfer between the metal ion and the hydroxide ion.

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CENTRAL RESEARCH DEPARTMENT, ST. LOUIS, MISSOURI

Exchange on Triply Connected Arsenic of the Substituents: Methoxyl, Dimethylamino, and the Halogens[1]

BY KURT MOEDRITZER AND JOHN R. VAN WAZER

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Proton nuclear magnetic resonance (n.m.r.) was used to study interchange of substituents in seven systems: *1,* $As(OCH_3)_3$ *vs.* $As[N(CH_3)_2]_3$; *2–4,* $As(OCH_3)$ *vs.* AsX_3; and *5–7,* $As[N(CH_3)_2]_3$ *vs.* AsX_3, where X stands for F, Cl, or Br. In addition, F^{19} n.m.r. was employed on the fluorine-containing compounds to check the reliability of the n.m.r. analytical procedure. In accord with previous work in our laboratory on exchange of these substituents on triply connected phosphorus and on silicon, it was found that the exchange equilibria of the methoxyl with the dimethylamino group do not deviate much from the values expected from ideal random sorting. On the other hand, there is a large deviation for the exchange of the dimethylamino group with halogens and a significant but lesser deviation for the exchange of methoxyl groups with halogens. These deviations are due to exothermic reactions between the end-member compounds to make the mixed species. For the arsenic systems, the values of ΔH corresponding to these nonrandom equilibria were measured calorimetrically and are compared herein with the ΔH values calculated from the deviations from randomness of the equilibrium constants. The rate of substituent interchange on the triply connected arsenic was found to be quite rapid in all cases. For all systems except $As(OCH_3)_3$–$As[N(CH_3)_2]_3$, the average rate of interchange was estimated as a function of concentration and temperature from the n.m.r. line shapes.

Previous studies[2] in this laboratory have indicated that exchange reactions of halogen atoms with either the dimethylamino or methoxyl group proceed to equilibrium points which deviate considerably from those corresponding to ideally random sorting of the substituents. It was postulated that the deviation from randomness, as measured by a free-energy difference, might in general be independent of the central atom to which these substituents are bonded, and this paper presents a test of this postulate for triply connected arsenic as the central atom.

In 1896, Michaelis and Luxembourg[3] described dialkylaminodichloroarsine. Articles[4] concerning this type of compound as well as bis(dialkylamino)chloroarsine have been published occasionally since that time. Although esters of arsenous acid were first investigated[5] nearly a century ago, the halo esters were apparently not studied[6] until fifty years later.

Experimental

Reagents.—Arsenic trifluoride was purchased from Chemical Procurement Laboratories (College Point 56, N. Y.), arsenic tribromide was from Bios Laboratories (New York 23, N. Y.), and arsenic trichloride was a Baker and Adamson reagent grade chemical. The arsenic halides were carefully redistilled in a dry nitrogen atmosphere before use. Tris(dimethylamino)arsine was made according to the procedure developed by one of us[7] and trimethyl arsenite was made as described below.

A 2-mole sample of arsenic trichloride was added slowly at a temperature of 5° to a well-stirred ice-cooled mixture consisting of 1.5 l. of *n*-hexane, 1.5 l. of diethyl ether, 6.5 moles of methanol, and 6.1 moles of triethylamine. After standing overnight, the solution was filtered and the solvent distilled off to give 236 g. (1.4 moles) of $As(OCH_3)_3$, b.p. 129–130° (760 mm.) (70% yield). A single sharp peak in the proton n.m.r. spectrum of the product indicated at least 99.5% purity with respect to hydrogen-containing materials. A qualitative test showed the absence of halogen in the product.

Equilibration.—Due to the hydrolytic sensitivity of the arsenic compounds, all materials were carefully handled in a nitrogen atmosphere in a drybox, having a dew point below −78°. Glassware was baked at 150° and cooled to room temperature *in vacuo*. Equilibration was carried out by either sealing the correct proportions of starting materials in glass tubes and heating to 120° for 5 days or by mixing the selected proportions of the starting ingredients and holding at 25° for 5 days. The same quantitative results were found in either case.

Analytical Procedures.—A Varian A-60 analytical n.m.r. spectrometer running at a frequency of 60 Mc. was employed for the H^1 n.m.r. determinations at room temperature. In general, a sweep rate of 0.1 c.p.s. was used at a sweep width of 50 cycles for full scan. The F^{19} n.m.r. determinations, as well as the H^1 spectra obtained at various temperatures, were run on a Varian HR-60 spectrometer at frequencies of 56.444 and 60.000 Mc., respectively. Spinning was not used in the F^{19} n.m.r. determinations since the samples were contained in 15-mm. o.d. Teflon tubes; but all samples determined by H^1 n.m.r. were spun in 5-mm. thin-walled precision-bore glass tubes.

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[1] Presented at the 144th National Meeting of the American Chemical Society, Los Angeles, Calif., April 2, 1963.

[2] (a) E. Fluck and J. R. Van Wazer, *Z. anorg. allgem. Chem.*, **307**, 113 (1961); J. R. Van Wazer and L. Maier, *J. Am. Chem. Soc.*, in press; (b) K. Moedritzer and J. R. Van Wazer, *J. Inorg. Nucl. Chem.*, in press; *Inorg. Chem.*, in press; also see (c) H. A. Skinner and N. B. Smith, *J. Chem. Soc.*, 2324, 3930 (1954).

[3] A. Michaelis and K. Luxembourg, *Ber.*, **29**, 710 (1896).

[4] G. A. Olah and A. A. Oswald, *Can. J. Chem.*, **38**, 1428, 1431 (1960); G. Kamai and Z. L. Khisamova, *Dokl. Akad. Nauk SSSR*, **105**, 489 (1955); *Zh. Obsch. Khim.*, **26**, 126 (1956).

[5] J. M. Crafts, *J. Chem. Soc.*, **24**, 817 (1871).

[6] A. McKenzie and J. K. Wood, *J. Chem. Soc.*, **117**, 406 (1920); L. Kolditz and D. Haas, *Z. anorg. allgem. Chem.*, **307**, 290 (1961).

[7] K. Moedritzer, *Chem. Ber.*, **92**, 2637 (1959).

TABLE I

OBSERVED N.M.R. CHEMICAL SHIFTS

Resonance obsd.	Substituent Z	Substituent T	Chemical shift in p.p.m. AsT_3	AsT_2Z	$AsTZ_2$	AsZ_3
F^{19a}	$N(CH_3)_2$	F	-36.5^b	-0.2^b	+44.2	
H^1 of $N(CH_3)_2{}^c$	$N(CH_3)_2$	F		-2.81^d	-2.66^e	−2.57
H^1 of $N(CH_3)_2{}^c$	$N(CH_3)_2$	Cl		−2.88	−2.71	−2.57
H^1 of $N(CH_3)_2{}^c$	$N(CH_3)_2$	Br		−2.85	−2.68	−2.55
H^1 of $N(CH_3)_2{}^c$	$N(CH_3)_2$	OCH_3		−2.67	−2.60	−2.55
H^1 of OCH_3	$N(CH_3)_2$	OCH_3	−3.52	−3.43	−3.38	
H^1 of OCH_3	OCH_3	Br		−3.94	−3.74	−3.57
H^1 of OCH_3	OCH_3	Cl		−3.94	−3.74	−3.57
H^1 of OCH_3	OCH_3	F		-3.79^f	-3.69^g	−3.57
F^{19}	OCH_3	F	−36.5	−12.0	+6.0	

[a] Referenced to trifluoroacetic acid, with samples measured as neat liquids. [b] Exchange between AsT_3 and AsT_2Z gave one peak at −23.3 p.p.m. for the over-all composition corresponding to $R \equiv F/As = 2.5$. [c] Referenced to tetramethylsilane, with samples measured in 10 volumes of CCl_4/volume of sample. [d] Spin–spin splitting gave a triplet, with $J_{F-H} = 3.8$ c.p.s. [e] Spin–spin splitting gave a doublet, with $J_{F-H} = 3.0$ c.p.s. [f] Broad line; splitting not resolved. [g] Spin–spin splitting gave a doublet, with $J_{F-H} = 1.0$ c.p.s.

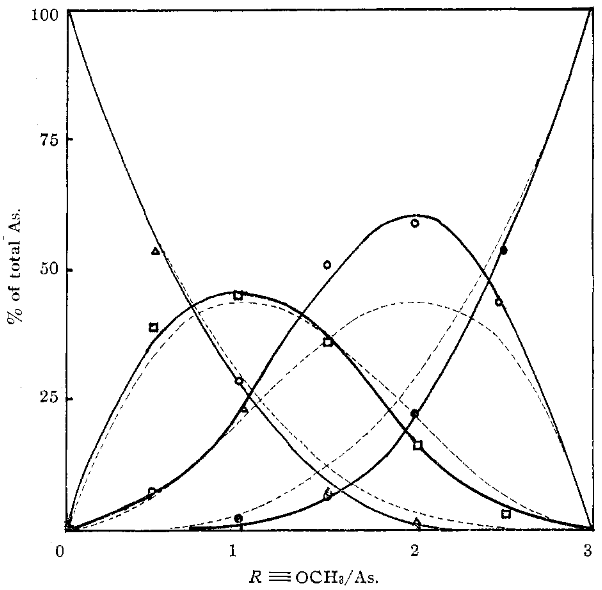

Fig. 1.—Equilibria at 25° for exchange of methoxyl for dimethylamino groups in the system $As(OCH_3)_3$–$As[N(CH_3)_2]_3$. The H^1 n.m.r. data from the methoxyl groups were consistent with that from the dimethylamino groups so that a single set of points is used to represent both measurements: △ = $As[N(CH_3)_2]_3$, □ = $CH_3OAs[N(CH_3)_2]_2$, ○ = $(CH_3O)_2AsN(CH_3)_2$, ● = $As(OCH_3)_3$.

Although the samples measured at 25° as neat liquids gave moderately broad but well-resolved resonance peaks in the F^{19} spectra, only a single, rather sharp line was observed for the neat liquids in the H^1 spectra of the systems involving AsF_3. Single peaks were also seen at 25° for the neat liquids in the systems $As(OCH_3)_3$–$AsBr_3$ and $As[N(CH_3)_2]_3$–AsX_3. However, upon dilution with carbon tetrachloride or other inert solvents, the single lines in these H^1 spectra broadened and finally formed multiplets. For the purpose of practical measurements on the spectra of the systems involving halogen atoms, the best results were obtained by dilution with ten parts by volume of CCl_4, since at this concentration resolution of the peaks was quite good and the peak areas were still large with respect to the errors introduced by spectrum "noise." Quantitative determinations of the molecular species present in the mixtures was made by integrating resonance peaks, using the integrator on the A-60 spectrometer for the H^1 spectra and weighing cut-out Xerox copies of the peaks for the F^{19} spectra.

The observed n.m.r. chemical shifts are presented in Table I where the reported assignments to the mixed-substituent molecules were made from inspection of spectra corresponding to various proportions of the substituents in the over-all mixtures and were checked by the stoichiometry of such mixtures. In the case of the H^1 spectra, a few drops of tetramethylsilane were added to the sample for referencing, and in the case of the F^{19} spectra, trifluoroacetic acid was the added reference. Negative shifts correspond to resonances downfield from the reference. As shown in Table I, spin–spin splitting was observed in the H^1 spectra. In the F^{19} spectra poorer resolution rendered unobservable spin–spin splitting. The fluorine–hydrogen coupling constant was found to be 3 to 4 c.p.s. as attenuated through the chain of three intermediate atoms As–N–C and *ca.* 1 c.p.s. as attenuated through the chain As–O–C.

Data and Interpretation

The experimental data obtained in this study are shown in Tables II and III and Fig. 1. The data in the two tables correspond to the exchange of either the dimethylamino or methoxyl group with fluorine, chlorine, and bromine, respectively. Figure 1 deals with the data for the dimethylamino–methoxyl exchange. It should be noted in Tables II and III that two sets of data are reported for each equilibration involving AsF_3: one from the H^1 and the other from the F^{19} n.m.r. measurements. The values given in parentheses in the tables and the curves of Fig. 1 were obtained[8] from the equilibrium constants calculated from the data.

These equilibrium constants are presented in Table IV, where independent values are given for the constants measured on the fluorine systems by the H^1 and F^{19} n.m.r. These values are seen to agree reasonably well and afford a good check of the reliability of n.m.r. for the quantitative analysis of mixtures.

As observed previously[2] it is found that the exchange of a halogen atom for a dimethylamino group is extremely nonrandom, with the mixed species being greatly preferred. The exchange of dimethylamino for methoxyl groups is again[2] quite close to randomness, with the halogen–methoxyl exchange lying between these two extremes.

Kinetic Measurements.—From our previous studies on exchange of the particular substituents[2] investigated

(8) L. C. D. Groenweghe, J. R. Van Wazer, and A. W Dickinson, *Anal. Chem.*, in press.

TABLE II

EQUILIBRIUM DATA FOR SUBSTITUENT INTERCHANGE IN THE SYSTEMS AsT_3–$As(OCH_3)_3$, T = F, Cl, Br, AT 37°

Mole ratio R = T/As	Mole percentage			
	$As(OCH_3)_3$	$TAs(OCH_3)_2$	T_2AsOCH_3	AsT_3
(a) The system AsF_3–$As(OCH_3)_3$ (T = F)[a]				
0.33	69.0	27.3	3.7	0.0
	(67.7)[b]	(30.8)	(1.5)	(0.0)
0.46	56.8	40.5	2.7	0.0
	(57.1)	(41.8)	(1.1)	(0.0)
0.76	32.8	57.4	9.8	0.0
	(31.9)	(60.9)	(8.2)	(0.0)
0.99	18.1	66.0	14.5	1.4
	(16.7)	(65.6)	(17.6)	(0.1)
1.28	9.3	59.3	25.1	6.3
	(6.9)	(58.7)	(34.0)	(0.4)
1.50	2.7	47.7	46.7	3.0
	(2.8)	(45.5)	(50.6)	(1.1)
1.76	0.2	26.4	70.7	2.8
	(0.7)	(26.1)	(69.5)	(3.7)
(b) The system AsF_3–$As(OCH_3)_3$ (T = F)[c]				
0.48	53.4	43.5	3.1	0.0
	(54.7)	(42.5)	(2.8)	(0.0)
0.99	18.6	63.9	17.2	0.3
	(19.7)	(63.8)	(16.4)	(0.1)
1.50	3.5	43.9	51.6	1.0
	(3.1)	(44.6)	(51.5)	(0.8)
1.98	0.0	11.0	80.8	8.2
	(0.1)	(10.6)	(80.5)	(8.8)
(c) The System $AsCl_3$–$As(OCH_3)_3$ (T = Cl)[a]				
0.50	50.9	47.5	1.6	0.0
	(50.4)	(49.2)	(0.4)	(0.0)
1.00	7.3	84.1	8.6	0.0
	(7.8)	(84.4)	(7.8)	(0.0)
1.26	0.9	71.6	27.5	0.0
	(1.6)	(70.7)	(27.7)	(0.0)
1.50	0.0	50.0	50.0	0.0
	(0.4)	(49.2)	(50.3)	(0.0)
1.75	0.0	24.9	75.1	0.1
	(0.1)	(25.0)	(74.7)	(0.2)
2.00	0.0	3.0	94.8	2.2
	(0.0)	(2.6)	(94.9)	(2.5)
2.49	0.0	0.0	50.7	49.3
	(0.0)	(0.0)	(50.9)	(49.1)
(d) The System $AsBr_3$–$As(OCH_3)_3$ (T = Br)[a]				
0.49	53.0	45.7	1.3	0.0
	(51.4)	(48.2)	(0.4)	(0.0)
0.97	10.0	77.5	3.6	0.0
	(10.0)	(83.1)	(6.9)	(0.0)
1.11	6.1	77.2	16.8	0.0
	(3.9)	(81.2)	(14.8)	(0.1)
1.51	2.4	36.9	59.2	1.5
	(0.4)	(48.8)	(49.3)	(1.5)
1.73	0.3	28.1	69.4	2.2
	(0.1)	(29.5)	(67.9)	(2.5)
2.00	0.0	10.3	79.6	10.0
	(0.0)	(10.0)	(80.0)	(10.0)
2.43	0.0	0.6	57.8	41.7
	(0.0)	(1.0)	(54.0)	(45.0)

[a] Data obtained from proton n.m.r. spectra. [b] Values calculated from equilibrium constants in Table IV. [c] Data obtained from F^{19} n.m.r. spectra.

here and on the polyarsenous oxyfluoride system,[9] one would expect the rate of substituent interchange in all cases to be quite fast (since arsenic atoms are involved), with the fastest rate corresponding to exchange of halogen atoms with dimethylamino groups and the slowest rate due to exchange of dimethylamino with methoxyl groups. This was found to be the case with the purified reagents carefully mixed and sealed in glass in a dry atmosphere. The faster exchanges were studied by H^1 n.m.r. line shapes which ranged from coalesced peaks, through partially separated peaks connected by saddles, to broadened separate peaks. In interpreting these data, we applied eq. 1–3 below[10] to compositions in the systems $As(OCH_3)_3$–AsX_3 and $As[N(CH_3)_2]_3$–AsX_3 selected so as to exhibit two equi-area peaks upon dilution. It is interesting to note that eq. 2 gave commensurate results whether or not the peaks were of equal area.

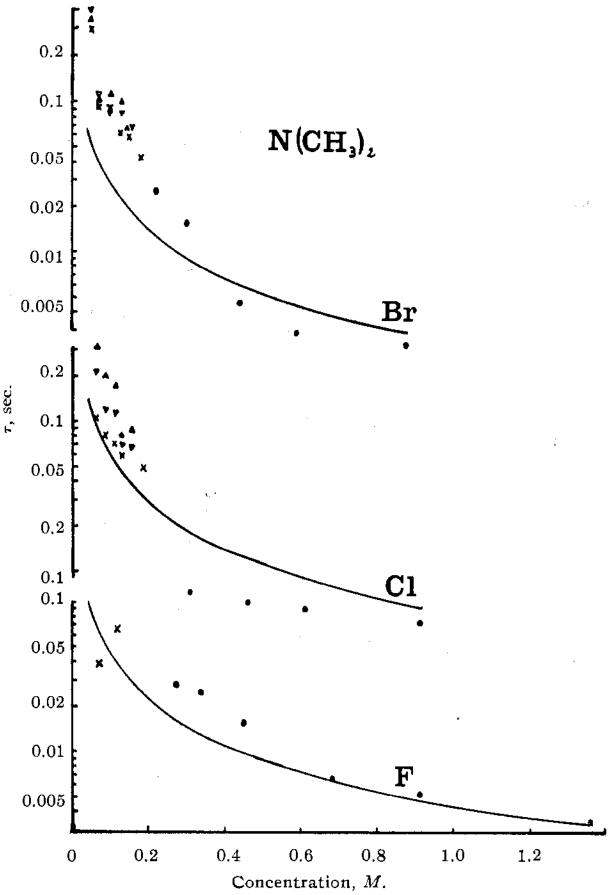

Fig. 2.—Variation at 25° of the calculated average lifetime, τ, of a given molecular species with respect to exchange of either fluorine, chlorine, or bromine atoms with the dimethylamino group when bonded to triply connected arsenic in an over-all composition exhibiting a halogen/arsenic mole ratio of 1.67. The dots, ●, correspond to measurements made from the broadening of completely coalesced proton n.m.r. peaks, using w_0 = 0.7 c.p.s.; the × to saddle-shaped peaks, and ▼▲ to the broadening of the downfield and upfield separated resonance peaks. The lines correspond to τC = constant and terminate at the high-concentration end of the reciprocal molar volume of the neat liquid.

Completely coalesced resonance peaks[10]

$$\tau = (w_o - w_o)/[B(\nu_{1\infty} - \nu_{2\infty})^2] \qquad (1)$$

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(9) K. Moedritzer, J. R. Van Wazer, and D. W. Matula, *J. Am. Chem. Soc.*, in press.

(10) J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High-Resolution Nuclear Magnetic Resonance," McGraw-Hill Book Co., New York, N. Y., 1959, pp. 220–225. See Fig. 10-1 on p. 223 for the values of *A* in eq. 3 of this paper.

Saddle-shaped spectra[10]

$$\tau = A/[2\pi(\nu_1 - \nu_2)] \qquad (2)$$

Separate resonances[10]

$$\tau = 1/[2\pi(w - w_0)] \qquad (3)$$

where τ is the average lifetime of an exchanging species in seconds, w_c is the width of the coalesced resonance peak in c.p.s. at half height, w is a similar measure but on a separated, broadened resonance peak, w_0 is a similar measure on the separated resonance peak under conditions where the exchange is sufficiently slow to not cause line broadening, $\nu_{1\infty}$ and $\nu_{2\infty}$ are the frequencies in c.p.s. of the separated lines when exchange is sufficiently slow so as not to cause line broadening, ν_1 and ν_2 are the frequencies of the neighboring lines under conditions where there is a saddle between them, B is a constant ranging from 4.9 for the coalescence of peaks of equal area to 4.0 for coalescence of peaks having areas in the ratio of 2:1, and A is a constant[10] ranging from 10 to 0.5 as the saddle between neighboring peaks becomes higher, with $A = \sqrt{2}$ when the saddle barely disappears to give a flat top due to peak coalescence.

TABLE III

EQUILIBRIUM DATA FOR SUBSTITUENT INTERCHANGE IN THE SYSTEM AsT_3–$As[N(CH_3)_2]_3$, T = F, Cl, Br, AT 37°

Mole ratio R = T/As	Mole percentage			
	$As[N(CH_3)_2]_3$	$TAs[N(CH_3)_2]_2$	$T_2AsN(CH_3)_2$	AsT_3
(a) The system AsF_3–$As[N(CH_3)_2]_3$ (T = F)[a]				
0.34	66.3	33.7	0.0	0.0
	(66.1)[b]	(33.6)	(0.3)	(0.0)
0.56	41.0	59.0	0.0	0.0
	(44.8)	(53.9)	(1.3)	(0.0)
0.78	19.7	80.3	0.0	0.0
	(25.1)	(71.6)	(3.3)	(0.0)
1.11	4.7	80.6	13.3	0.0
	(5.6)	(79.9)	(15.5)	(0.0)
1.32	2.1	57.8	40.1	0.0
	(1.8)	(64.2)	(34.0)	(0.0)
1.54	0.0	44.7	55.3	0.0
	(0.6)	(45.0)	(54.5)	(0.0)
1.78	0.0	20.9	79.1	0.0
	(0.1)	(21.8)	(78.1)	(0.0)
2.00	0.0	0.0	100.0	0.0
	(0.0)	(0.0)	(100.0)	(0.0)
(b) The system AsF_3–$As[N(CH_3)_2]_3$ (T = F)[c]				
0.54	47.3	51.4	1.2	0.0
	(46.0)	(54.0)	(0.0)	(0.0)
1.12	0.0	86.2	13.7	0.0
	(0.2)	(87.7)	(12.2)	(0.0)
1.47	0.0	59.9	46.1	0.0
	(0.0)	(53.0)	(47.0)	(0.0)
2.00	0.0	0.0	100.0	0.0
	(0.0)	(0.0)	(100.0)	(0.0)
(c) The system $AsCl_3$–$As[N(CH_3)_2]_3$ (T = Cl)[a]				
0.48	56.9	43.1	0.0	0.0
	(52.0)	(48.0)	(0.0)	(0.0)
1.01	0.3	98.1	1.5	0.0
	(0.6)	(97.6)	(1.8)	(0.0)
1.18	0.5	81.9	17.6	0.0
	(0.0)	(82.0)	(18.0)	(0.0)
1.52	0.0	46.5	53.5	0.0
	(0.0)	(48.0)	(52.0)	(0.0)
1.78	0.0	18.7	81.3	0.0
	(0.0)	(22.0)	(78.0)	(0.0)
2.02	0.0	0.3	97.6	2.1
	(0.0)	(0.6)	(97.2)	(2.1)
2.50	0.0	0.0	49.6	50.4
	(0.0)	(0.0)	(50.0)	(50.0)
(d) The system $AsBr_3$–$As[N(CH_3)_2]_3$ (T = Br)[a]				
0.52	46.2	53.8	0.0	0.0
	(52.0)	(48.0)	(0.0)	(0.0)
1.00	0.8	99.2	0.0	0.0
	(0.1)	(99.8)	(0.1)	(0.0)
1.26	0.4	73.3	26.3	0.0
	(0.0)	(74.0)	(26.0)	(0.0)
1.51	0.0	49.0	51.0	0.0
	(0.0)	(49.0)	(51.0)	(0.0)
1.77	0.0	21.5	78.5	0.0
	(0.0)	(23.0)	(77.0)	(0.0)
2.00	0.0	0.5	99.4	0.1
	(0.0)	(0.3)	(99.5)	(0.2)
2.51	0.0	0.0	51.5	48.5
	(0.0)	(0.0)	(49.0)	(51.0)

[a] Data obtained from proton n.m.r. spectra. [b] Values calculated from equilibrium constants in Table IV. [c] Data obtained from F^{19} n.m.r. spectra.

TABLE IV

EQUILIBRIUM CONSTANTS FOR SUBSTITUENT INTERCHANGE AT 37°

Substituents		$K_1 = \frac{[AsTZ_2][AsT_3]}{[AsT_2Z]^2}$	$K_2 = \frac{[AsZ_3][AsT_2Z]}{[AsTZ_2]^2}$
Z	T		
$N(CH_3)_2$	F	*ca.* 10^{-8}, $\sigma^a = 4 \times 10^{-6}$	1.6×10^{-2}, $\sigma = 0.5 \times 10^{-2}$
$N(CH_3)_2$	F^b	*ca.* 10^{-8}, $\sigma = 2 \times 10^{-6}$	*ca.* 10^{-4}, $\sigma = 0$
$N(CH_3)_2$	Cl	6×10^{-5}, $\sigma = 2 \times 10^{-4}$	6×10^{-5}, $\sigma = 1.5 \times 10^{-4}$
$N(CH_3)_2$	Br	6×10^{-6}, $\sigma = 3 \times 10^{-5}$	6×10^{-7}, $\sigma = 5 \times 10^{-5}$
$N(CH_3)_2$	OCH_3	0.095, $\sigma = 0.004$	0.314, $\sigma = 0.012$
OCH_3	F	0.019, $\sigma = 0.015$	0.068, $\sigma = 0.007$
OCH_3	F^b	0.0138, $\sigma = 0.0008$	0.080, $\sigma = 0.003$
OCH_3	Cl	7.3×10^{-4}, $\sigma = 0.6 \times 10^{-4}$	0.0859, $\sigma = 0.0011$
OCH_3	Br	0.016, $\sigma = 0.003$	0.009, $\sigma = 0.003$

[a] σ is the standard deviation of the constants. [b] Data from F^{19} n.m.r. measurements at a temperature of 28°; all others from H^1 n.m.r. at 37°.

Figure 2 shows the variation with concentration of the average lifetime for exchange of dimethylamino groups with halogen atoms in a mixture consisting predominantly of dihalodimethylaminoarsine and halobis(dimethylamino)arsine, which was diluted with carbon tetrachloride (with the over-all composition set at $R \equiv$ T/As = 1.67 in all cases, for T representing the halogen). In this figure the concentrations are given in moles per liter and range from the neat liquids to dilutions with 15–20 parts of CCl_4. The curves shown in this figure correspond to a constant product of the average lifetime, τ, multiplied by the concentration, C, a situation which is to be expected for a second-order reaction. It should be noted that the data of Fig. 2 agree reasonably well with this type of concentration dependence. The average lifetime for exchange of bromine atoms with dimethylamino groups seems to change more rapidly than expected for a constant value of τC so that a reaction order greater than two is indicated.

A similar set of curves may be obtained for the methoxyl–halogen exchange, again for $R \equiv$ T/As = 1.67. For the neat liquids, the lifetime for exchange of the methoxyl group with Br is 0.03 sec.; with Cl, 0.07 sec.; and with F, 0.005 sec.

In Fig. 2, the rate of exchange of a halogen atom for a dimethylamino group is shown to change very little when going from one halogen to another, whereas the room-temperature exchange of halogens for methoxyl groups in the neat liquids is in the order of descending reaction velocities: F > Br > Cl, with about a fourfold increase per step. The main difference, when changing from dimethylamino to methoxyl, is a decrease of about tenfold in the rates of exchange with chlorine and with bromine. It is, of course, quite reasonable to assume that the observed differences in rates when going from one halogen to another may be due in part (or even completely) to variations in trace amounts of catalytic impurities. Therefore we can only conclude that, without much question, the exchange of fluorine, chlorine, or bromine with either the methoxyl or dimethylamino group on triply connected arsenic is rapid, corresponding to second-order rate constants of the order of magnitude of 10^2 l./sec.-mole.

Temperature measurements on the neat liquids show that, for exchange of halogen with the methoxyl group, the activation energy is relatively low (E = *ca.* 2 kcal.) and is reasonably independent of the halogen employed. Similarly, exchange of either chlorine or bromine for the dimethylamino group in the neat liquids gives the same activation energy of 5 kcal. An interesting anomaly was noted in the temperature dependence of the exchange of bromine atoms for methoxyl groups, as shown in Fig. 3. It was found that the average lifetime first increased in the normal manner with decreasing temperature and then some other process took over to cause the peaks to coalesce.

The room-temperature H^1 n.m.r. spectra of mixtures of arsenic trifluoride with either trimethyl arsenite or tris(dimethylamino)arsine as neat liquids gave single coalesced resonances; whereas, the F^{19} n.m.r. spectra gave well-resolved peaks. This great difference in the appearance of the H^1 and F^{19} spectra is in accord with eq. 1 and 3 because the chemical shift between the fluorine resonances is so great that the denominator of eq. 2 becomes very large, thus making eq. 3, as the limiting case of eq. 2, apply to the same exchange rates in the case of the F^{19} spectra as does eq. 1 in the case of the H^1 spectra.

The rate of exchange of methoxyl for dimethylamino groups in the neat liquid was too slow to measure by n.m.r. line broadening and too fast to study by a timed run. However, the rate was sufficiently retarded by dilution of the two reactants in five parts of CCl_4, with precautions to preserve purity, so that kinetic measurements could be made at room temperature over the period of time of an hour or so. A typical kinetic run is shown in Fig. 4, from which it can be seen that τ, the average lifetime for substituent exchange (*i.e.*, the time for the species to achieve $1/e$ of their equilibrium value) in this dilute solution at 37° is *ca.* 10 min.—a value which is 10^4–10^5 times greater than the average lifetime for exchange of halogens with either the methoxyl or dimethylamino groups.

Enthalpy Measurements.—Since the exchange of halogens with either the methoxyl or dimethylamino group was rapid, as shown by Fig. 2, calorimetric measurements of the heats of the reactions could be made with a simple arrangement of dewar flask and Beckmann thermometer. Usually the arsenic trihalide was mixed with either trimethyl arsenite or the tris(dimethylamino)arsine in the mole proportions of 1:2 and 2:1. However, in the case of $AsCl_3$ or $AsBr_3$ *vs.* $As[N(CH_3)_2]_3$, a number of different stoichiometric combinations were studied, as indicated in footnote *b* of Table V. When the respective equilibrium constants of Table IV were such that the 2:1 or 1:2 combinations of starting ingredients corresponded to mixtures of compounds at equilibrium, the heats of formation of the pure mixed species were calculated by means of simultaneous equations from the measured heats to give the results shown in Table V. It should be noted in this table that all measurements except those involving bromine were taken at 25°. Because $AsBr_3$ melts at 36°, the calorimetric measurements involving exchange of bromine atoms were made at 40° and hence are subject to greater error than the other measurements.

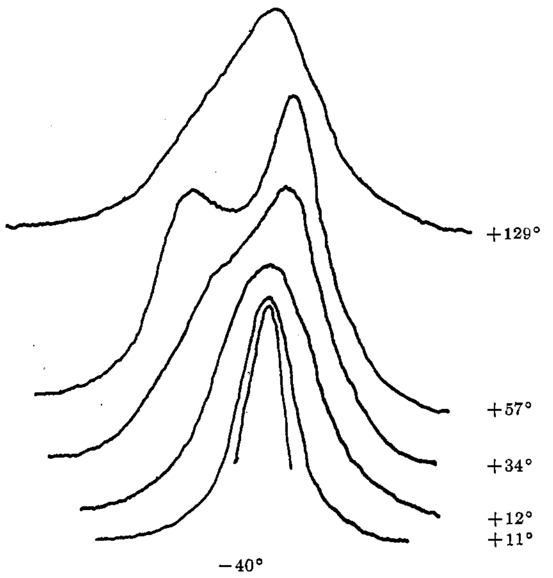

Fig. 3.—Line shapes as a function of temperature in the proton n.m.r. spectrum of the composition for which $R \equiv Br/As = 1.67$ in the system $AsBr_3$–$As(OCH_3)_3$.

TABLE V

ENTHALPIES FOR FORMATION OF MIXED COMPOUNDS FROM THE END MEMBERS

	−Δ in kcal./mole					
	T = F		T = Cl		T = Br[c]	
$As[N(CH_3)_2]T_2$	3.6	(*ca.* 7)[a]	6.9[b]	(5.5)	6 to 7[b]	(7.3)
$As[N(CH_3)_2]_2T$	2.0	(*ca.* 5)	6.8[b]	(5.5)	7 to 9[b]	(7.7)
$As(OCH_3)T_2$	2.4	(1.5)	3.8	(2.6)	2.2	(1.9)
$As(OCH_3)_2T$	1.7	(1.2)	3.4	(1.8)	2.2	(2.0)

[a] Values in parentheses were calculated from the equilibrium constants on the assumption that the entropy is entirely attributable to the "entropy of mixing." [b] Best value corresponding to the set of reactions: *1*, $2AsZ_3 + AsT_3$; *2*, $AsZ_3 + 2AsT_3$; *3*, $AsZ_3 + AsT_2Z$; and *4*, $AsTZ_2 + AsT_3$, for all of which ΔH values were measured. [c] Calorimetric measurements made at 40°.

The values of ΔH given in parentheses in Table V were estimated by calculating (in terms of free energy) the deviations from randomness of the equilibrium constants of Table IV. In all cases, the enthalpies as directly measured agree reasonably well with those calculated from the equilibrium constants on the assumption that the entropy of the exchange reaction

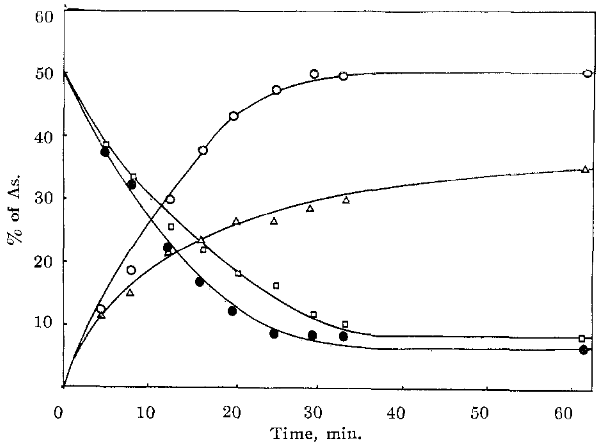

Fig. 4.—The kinetics of the reaction of molar quantities of $As(OCH_3)_3$ and $As[N(CH_3)_2]_3$ diluted with 5 volumes of CCl_4 at 37°: ○, $As(OCH_3)_2[N(CH_3)_2]$; △, $As(OCH_3)[N(CH_3)_2]_2$; □, $As[N(CH_3)_2]_3$; ●, $As(OCH_3)_3$.

is due solely to the entropy of mixing[11] (*i.e.*, random interchange).

Conclusions

Large negative enthalpy contributions to the free energy are found in the exchange of dimethylamino groups for halogens on arsenic. Also, the enthalpies for exchange of methoxyl groups for halogens on arsenic are large enough negative values to give significantly nonrandom equilibria but are smaller than those found for the dimethylamino–halogen exchanges. However, the relation between Hammett σ_m constants and the free-energy deviations from ideality suggested for exchange reactions on silicon[2b] is seen to be invalid, at least in this case, since the exchange of the methoxyl for the dimethylamino group is quite close to random on the triply connected arsenic and the methyl- and dimethylsilicon moieties. Since it has been shown for P,[2a], Si[2b], B,[2c] and now As that halogen *vs.* dimethylamino exchange gives the mixed species in nearly stoichiometric amounts at equilibrium, it seems reasonable to conclude that this extreme nonrandom behavior is independent of the central atom. A similar generality seems to apply to the lesser nonrandom behavior of halogen *vs.* methoxyl exchange.

As would be expected for a third-row element, the rates of exchange of the substituents studied here are all fast. The tremendous increase in rate of exchange of halogens with either the methoxyl or dimethylamino groups as compared to exchange of methoxyl with dimethylamino is probably attributable to the influence of the large enthalpies of the exchange reactions in reducing the activation energies.[12]

In view of the fact that the rate of exchange of dimethylamino groups with fluorine is extremely rapid at room temperature, the isolation by distillation of dialkylaminodifluoroarsines by Olah and Oswald[4] is noteworthy. We repeated their work and, in addition, distilled this compound without decomposition under atmospheric pressure at a rate of 5 ml./hr. in a still having 20–30 theroetical plates. Under the same conditions, the bis(dimethylamino)fluoroarsine separated very cleanly into equimolar amounts of dimethylaminodifluoroarsine and tris(dimethylamino)arsine. In spite of the fast rate of substituent exchange, the free energy of formation of the dimethylaminodifluoroarsine from the mono and trifluoro compounds has a sufficiently large negative value so that the equilibrium mixture of arsenic trifluoride and bis(dimethylamino)fluoroarsine is not present in amounts which can be separated under the conditions of distillation employed.

It should be noted that the few mixed-substituent *neso* compounds described in the previous literature on arsenic appear to be either compounds which are present to very large amounts at equilibrium or are solids. Likewise, the few molecules based on more than one arsenic atom that have been reported prior to our studies are relatively slow to exchange (cocodyl and its derivatives, which have relatively slowly reorganizing bonds or carbons) or are solids in which reorganization is inhibited by diffusion. In this respect, the chemistry of arsenic is similar to many of the other heavy elements and mixed compounds cannot be isolated (*i.e.*, "prepared") by standard methods unless the substituent-exchange reactions are either highly exothermic or suitably slow.

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[11] J. R. Van Wazer, D. W. Matula, and L. C. D. Groenweghe, *J. Chem. Phys.*, to be submitted. Also see J. R. Van Wazer, *Am. Scientist*, **50**, 450 (1962).

[12] G. S. Hammond, *J. Am. Chem. Soc.*, **77**, 334 (1955). This theorem was first proposed by Polanyi; L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., New York, N. Y., 1940, pp. 136–138.