Substitution at Saturated Carbon. Part XVIII.[1] The Effect of Alcoholic Solvents on Rate Constants for S_N and S_E Reactions

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Rate constants are reported for reactions between the following nine pairs of reactants, using a number of pure alcohols as solvents: Et_3N and EtI, Pr^n_3N and MeI, Me_4Sn and $HgCl_2$, Me_4Sn and HgI_2, Et_4Sn and $HgCl_2$, Et_4Sn and HgI_2, Et_4Sn and $Hg(OAc)_2$, Me_4Sn and I_2, and Et_4Sn and I_2. Comparisons have been carried out between the effect of alcoholic solvents on $\Delta G^\ddagger$ values for 21 S_N and S_E reactions, and it is shown that no simple solvent parameter can adequately correlate such solvent effects on the various reactions. However, in general, the retarding effect of the less polar alcohols on the organometallic substitutions lies between the very large solvent effect on the S_N1 reaction of t-butyl halides and the much smaller solvent effect on the S_N2 Menschutkin reactions. The reaction between Et_3N and EtI and that between Pr^n_3N and MeI are anomalous in that molar rate constants in t-butyl alcohol are as high as rate constants in the much more polar solvent methanol.

In previous work, we have compared the effects of methanol–water solvents on a typical S_E2 aliphatic electrophilic substitution with such effects on S_N1 and S_N2 reactions. For the S_E2 reaction and the S_N reactions, added water promotes an increase in the reaction rate constant largely by destabilising the reactants.[2,3] On the other hand, addition of the less polar t-butyl alcohol solvent to methanol produces a decrease in the S_E2 rate constant mainly by raising the free energy of the transition state.[4] Although this type of behaviour is similar to that found in S_N1 reactions of t-butyl halides in various pure alcohol solvents,[5] there is but little direct comparison that can be made between the effect of nonaqueous alcoholic solvents on rate constants for typical S_N and S_E reactions. We have therefore determined rate constants for a number of S_N and S_E reactions, using pure alcohols as the solvents, in order to provide such a comparison.

The S_N2 *Menschutkin Reaction.*—The solvolysis of t-butyl chloride has long been the reference reaction in studies of solvent effects on reaction rate constants,[6] but more recently it has been suggested [7] that the S_N2 Menschutkin reaction of tertiary amines with alkyl halides would also be a suitable reference reaction. Only few studies have been carried out on the classic triethylamine–ethyl iodide reaction at ambient temperatures, and so we determined rate constants for reaction (1) at 298 K using a number of pure alcohols as solvents. Details of the rate measurements are in the Experimental section; all reactions yielded good second-order kinetic plots, with a second-order rate constant invariant over a range of initial concentrations of reactants. In most of the alcohols, the product salt precipitated out during the course of reaction, but the rate constant calculated from data up to the time of precipitation was identical to that calculated from data at later reaction times. Average values of the rate constant from 8—10 kinetic runs in each case together

$$Et_3N + EtI \longrightarrow Et_4N^+I^- \qquad (1)$$

with the variance ($v\% = 100\sigma/k$, where σ is the standard deviation and k the average value of the rate constant) are in Table 1; there is good agreement with previous results [8,9] for methanol solvent, but only fair agreement with the early work of Eagle and Warner [10] for ethanol solvent. Interestingly, the rate constant for reaction (1) in propan-2-ol and in t-butyl alcohol is higher than expected; indeed, the value of the rate constant in t-butyl alcohol of dielectric constant $\varepsilon^{25} = 12{\cdot}5$ is higher than in methanol, $\varepsilon^{25} = 32{\cdot}6$. Since this is an unexpected (and unique) result, we also carried out rate measurements on the related reaction (2), using propan-1-ol, propan-2-ol, and t-butyl alcohol as solvents.

$$Pr_3N + MeI \longrightarrow Pr_3N^+MeI^- \qquad (2)$$

Values of the rate constant are in Table 1; our value for reaction in propan-1-ol agrees well with that of Lassau and Jungers.[11] Once again rate constants in propan-2-ol and especially in t-butyl alcohol are higher than expected, so that the two simple Menschutkin reactions (1) and (2) cannot be regarded as satisfactory indicators of solvent polarity as far as the alcoholic solvents in Table 1 are concerned.

The S_E2 *Reactions of Tetra-alkyltins with Mercury*(II) *Salts.*—In earlier work [1,12-14] we have determined rate

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[1] Part XVII, M. H. Abraham and D. F. Dadjour, *J.C.S. Perkin II*, 1974, 233.

[2] M. H. Abraham and G. F. Johnston, *J. Chem. Soc.* (*A*), 1971, 1610.

[3] M. H. Abraham, *J. Chem. Soc.* (*A*), 1971, 1061.

[4] M. H. Abraham and F. J. Dorrell, *J.C.S. Perkin II*, 1973, 444.

[5] M. H. Abraham, *J.C.S. Perkin II*, 1972, 1343.

[6] E. Grunwald and S. Winstein, *J. Amer. Chem. Soc.*, 1948, **70**, 846.

[7] Y. Drougard and D. Decroocq, *Bull. Soc. chim. France*, 1969, 2972; K. F. Wong and C. A. Eckert, *Ind. Eng. Chem.*, 1970, **62** (No. 9), 16.

[8] Professor Y. Kondo, personal communication.

[9] H. Hartmann, H. D. Brauer, and G. Rinck, *Z. phys. Chem.* (*Frankfurt*), 1968, **61**, 47.

[10] S. Eagle and J. C. Warner, *J. Amer. Chem. Soc.*, 1939, **61**, 488.

[11] C. Lassau and J.-C. Jungers, *Bull. Soc. chim. France*, 1968, 2678.

[12] M. H. Abraham and P. L. Grellier, *J.C.S. Perkin II*, 1973, 1132.

[13] M. H. Abraham and F. Behbahany, *J. Chem. Soc.* (*A*), 1971, 1469.

[14] M. H. Abraham, F. Behbahany, and M. J. Hogarth, *J. Chem. Soc.* (*A*), 1971, 2566.

constants for reaction (3; R = Me or Et; X = Cl, I, or OAc) in solvents methanol and t-butyl alcohol, and have

$$R_4Sn + HgX_2 \longrightarrow RHgX + R_3SnX \qquad (3)$$

now extended these measurements to solvents ethanol, propan-1-ol, and butan-1-ol. Details are in the Experimental section, and in Table 2 are summarised results to date. For reaction of mercury(II) acetate in methanol, it is known[1] that the rate constant for reaction of the species $Hg(OAc)_2$ is less than the observed rate constant, and in Table 2 we have estimated the 'true' rate constant by comparison with previous data.[1] In the case of mercury(II) acetate reactions in the other alcohols, it is likely that the true rate constant is much closer to the observed rate constant, and we have taken the observed values as approximately equal to the true constants.

TABLE 1

Rate constants for the reaction of triethylamine with ethyl iodide and of tri-n-propylamine with methyl iodide

	MeOH	EtOH	Pr^nOH	Pr^iOH	Bu^nOH	Bu^tOH
A $Et_3N + EtI$ at 298 K						
k ($l\ mol^{-1}\ h^{-1}$) [a]	0·0140 [b]	0·0118 [c]	0·00858	0·0115	0·00697	0·0162
variance (v%)	4·8	2·5	4·2	2·7	3·5	3·0
relative k	100	84	61	82	50	116
B $Pr_3N + MeI$ at 293 K						
k ($l\ mol^{-1}\ min^{-1}$)	0·0130 [d]	0·0095 [d]	0·0073 [e]	0·0076 [f]	0·0046 [d]	0·0130 [f]
relative k	100	73	56	58	35	100

[a] Average values from 8—10 kinetic runs (this work). [b] Reported values are 0·0140 (ref. 8) and 0·0142 (from extrapolation of data in ref. 9). [c] Ref. 10 gives 0·0096 l mol^{-1} h^{-1}. [d] Ref. 11. [e] Average value from this work (0·0072) and ref. 11 (0·0074). [f] This work.

TABLE 2

Rate constants ($l\ mol^{-1}\ min^{-1}$) for the reaction of tetra-alkyltins with mercury(II) salts at 298 K [a]

Reactants	MeOH	EtOH	Pr^nOH	Bu^nOH	Bu^tOH
$Me_4Sn + HgCl_2$	93·1 [b]	50·85	42·52	31·72	6·21 [c]
$Me_4Sn + HgI_2$	18·6 [d]	9·26	5·65	4·49	0·42 [e]
$Me_4Sn + Hg(OAc)_2$	6400 [f]				49·7 [g]
$Et_4Sn + HgCl_2$	0·200 [b,h]	0·0745	0·0594	0·0471	0·0069 [h]
$Et_4Sn + HgI_2$	0·152 [h]	0·0581	0·0369	0·0272	0·0019 [h]
$Et_4Sn + Hg(OAc)_2$	28·0 [f]	14·29	13·66	12·10	0·46 [h]

[a] This work except where indicated. [b] Ref. 30. [c] Ref. 14. [d] Personal communication from Miss J. H. Andonian. [e] Estimated value from other data in Bu^tOH. [f] Approximate values for the rate constant for the species $Hg(OAc)_2$, see refs. 1 and 12. [g] Observed rate constant, ref. 12. [h] Ref. 13.

TABLE 3

The ratio $k(Me_4Sn)/k(Et_4Sn)$ for reaction with mercury(II) salts at 298 K [a]

Salt	MeOH	EtOH	Pr^nOH	Bu^nOH	Bu^tOH
$HgCl_2$	466	682	715	673	900
HgI_2	122	159	153	165	220
$Hg(OAc)_2$	228				108

[a] Data from Table 2.

It has been suggested[15] that there is a correlation between values of $k(Me_4Sn)/k(Et_4Sn)$ for reaction (3) and the extent of charge separation in the transition state. In Table 3 are the various rate constant ratios observed; it is clear that for reaction (3; X = Cl and I) there is no reduction in charge separation as the alcohol solvent becomes less polar. However, the ratio $k(Me_4Sn)/k(Et_4Sn)$ for the acetate reaction is less in t-butyl alcohol than in methanol, so that it is possible for the transition state to be less polar in t-butyl alcohol than in methanol solvent. The same conclusion may be drawn from the relative reactivities of the three mercury(II) salts as shown in Table 4. Only for the reaction of mercury(II) acetate in t-butyl alcohol is it likely that the transition state is less polar than it is in methanol.

Iododemetallation of Tetra-alkyltins.—Although halogenodemetallations have been extensively studied, rate constants for reactions in a number of alcoholic solvents are known only for iododemetallation of tetramethyl- and tetraethyl-lead (solvents were MeOH, EtOH, and

TABLE 4

Relative reactivities of mercury(II) salts towards tetra-alkyltins at 298 K [a]

	With Et_4Sn			With Me_4Sn		
	$Hg(OAc)_2$	$HgCl_2$	HgI_2	$Hg(OAc)_2$	$HgCl_2$	HgI_2
MeOH	140	1	0·76	69	1	0·20
EtOH	192	1	0·78		1	0·18
Pr^nOH	230	1	0·62		1	0·13
Bu^nOH	257	1	0·58		1	0·14
Bu^tOH	67	1	0·28	8	1	0·07

[a] Data from Table 2.

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[15] M. H. Abraham and M. J. Hogarth, *J. Chem. Soc.* (*A*), 1971, 1474.

Pr^nOH).[5,16] In order to provide further data we have determined rate constants for reaction (4; R = Me and Et). Iododemetallations in polar solvents are usually

$$R_4Sn + I_2 \longrightarrow RI + R_3SnI \qquad (4)$$

carried out in presence of iodide ion in order to convert nearly all the iodine into the I_3^- ion. Under these conditions the second-order rate constant for reaction (4) is given[17,18] by $k_2 = k_2^{obs}K[I^-]$ where k_2^{obs} is the observed second-order rate constant, K is the formation constant for the species I_3^-, and $[I^-]$ is the concentration of iodide ion present. Thus a knowledge of the formation constant K is necessary for the evaluation of the rate constant for reaction (4). Fortunately, values of K in ethanol and propan-1-ol at 298 K and ionic strength (μ) = 10^{-3}—10^{-4}M are known,[16] a value in propan-2-ol at 298 K is available,[19] and a value of K in methanol at 298 K and ionic strength 10^{-3}M can be deduced [*] from measurements made by Nasielski and his co-workers.[17,20] In Table 5 are details of the rate constants for reaction (4; R = Me and Et) using four alcohols as solvents; it should be noted that these rate constants include uncertainties in the values of the equilibrium constants as well as in the rate measurements. Our present values of the rate constant for reaction (4; R = Me and Et) in methanol at 298 K and μ = 10^{-3}M are in reasonable agreement with values obtained by Gielen and Nasielski[17,21] under slightly different conditions. These workers have suggested that the rate constant ratio $k(Me_4Sn)/k(Et_4Sn)$ for iododemetallations reflects the polarity of the solvent, the lower the ratio the less polar the solvent. Values of this ratio are in Table 6 and show, at least for iododemetallation of tetra-alkyltins, that the ratio does tend to decrease as the alcohol solvent becomes less polar.[†]

TABLE 5

Rate constants for the iododemetallation of tetra-alkyltins at 298 K

	MeOH	EtOH	Pr^nOH	Pr^iOH
$K(I_3^-)$ [a] (l mol^{-1})	1·57 × 10^4 [c]	3·32 × 10^4	2·48 × 10^4	2·09 × 10^5
$k(Me_4Sn)$ [b] (l mol^{-1} s^{-1})	6·84 (1%)	1·325 (1%)	0·438 (3%)	0·476 (4%)
$k(Et_4Sn)$ [b] (l mol^{-1} s^{-1})	1·26 (1%)	0·265 (3%)	0·095 (7%)	0·170 [d]

[a] Formation constants for I_3^- from refs. 16, 17, 19, and 20 (see text). [b] This work, using 1·00 × 10^{-3}M-Bu_4NI; the variance (in parentheses) does not include the errors in values of $K(I_3)$. [c] A value of 1·60 × 10^4 (after conversion to the molar scale) at 298 K and zero ionic strength is given by F. G. K. Baucke, R. Bertram, and K. Cruse, *J. Electroanalyt. Chem. Interfacial Electrochem.*, 1971, **32**, 247. [d] Approximate value only.

Comparison between Various Substitution Reactions.— First-order rate constants for the solvolysis of t-butyl chloride and t-butyl bromide are available,[5] and those for the solvolysis of benzyl bromide may be calculated from the second-order rate constants given by Murgulescu and Demetrescu.[22] In Table 7 are given values of $\delta\Delta G^\ddagger = \Delta G^\ddagger$ (alcohol solvent) $- \Delta G^\ddagger$ (methanol solvent) for these S_N solvolyses, for iododemetallations of tetra-alkyltins and tetra-alkyl-leads, for the S_E2 substitution of tetra-alkyltins by mercury(II) salts, and for the S_N2 substitutions of alkyl halides by tertiary amines. In the calculation of the $\Delta G^\ddagger$ values, all second-order rate constants have been converted to units of mol-fraction^{-1} s^{-1}.

The 21 reactions detailed in Table 7 are all examples of substitution reactions in which relatively nonpolar reactants proceed to more polar transition states. Since these reactions have been examined in a series of structurally related solvents, they might well be expected to follow some parameter of solvent polarity through a set of linear free energy relationships. However, in general the values of $\delta\Delta G^\ddagger$ for the different reactions are not linearly related, and hence there can be no simple solvent parameter that will adequately correlate values of $\delta\Delta G^\ddagger$ for all the various substitution reactions in the alcoholic solvents. Although it is therefore difficult to make any quantitative assessment of the relative magnitude of the solvent effect on the values of $\Delta G^\ddagger$ for the 21 reactions, inspection of Table 7 suggests the following qualitative order (reactants are

TABLE 6

The ratio $k(Me_4M)/k(Et_4M)$ for iododemetallation at 298 K

M	MeOH	EtOH	Pr^nOH	Pr^iOH
Sn [a]	5·43 [b]	5·00	4·61	2·8 [c]
Pb [d]	2·57 [e]	2·10	2·21	

[a] This work, rate constants from Table 5. [b] 8·5 and 8·0 at 293 K, refs. 17 and 21. [c] Approximate value. [d] Ref. 16. [e] 2·83 at 293 K (M. Gielen and J. Nasielski, *J. Organometallic Chem.*, 1967, **7**, 273).

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[*] Values of K are given[17] as 1·89 × 10^4 (μ = 8 × 10^{-5}M) and 2·04 × 10^4 (μ = 0·005—0·20M) at 293 K; when combined with earlier data[20] on the temperature variation of K, a value of 1·57 × 10^4 at 298 K and ionic strength 10^{-3}—10^{-4}M may be calculated.

[†] Note that we regard the value of $k(Me_4Sn)/k(Et_4Sn)$ for reaction (3) as a reflecting the polar character of the transition state, whereas Gielen and Nasielski use this ratio for reaction (4) as a measure of the polar character of the solvent.

[16] L. Riccoboni, G. Pilloni, G. Plazzogna, and G. Tagliavini, *J. Electroanalyt. Chem. Interfacial Electrochem.*, 1966, **11**, 340.

[17] M. Gielen and J. Nasielski, *Bull. Soc. chim. belges*, 1962, **71**, 32.

[18] M. H. Abraham, ' Electrophilic Substitution at a Saturated Carbon Atom,' in ' Comprehensive Chemical Kinetics,' eds. C. H. Bamford and C. F. H. Tipper, Elsevier, *Amsterdam*, 1973, vol. 12.

[19] J. Nasielski, O. Buchman, M. Grosjean, and E. Hannecart, *Bull. Soc. chim. belges*, 1968, **77**, 15.

[20] O. Buchman, M. Grosjean, and J. Nasielski, *Helv. Chim. Acta*, 1964, **47**, 1679.

[21] S. Boué, M. Gielen, and J. Nasielski, *J. Organometallic Chem.*, 1967, **9**, 443.

[22] I. G. Murgulescu and I. Demetrescu, *Rev. Roumaine Chim.*, 1970, **15**, 141; 1972, **17**, 595.

given): $\mathrm{Bu^tCl > R_4Sn/I_2 > R_4Pb/I_2 \geqslant R_4Sn/HgX_2 > PhCH_2Br \geqslant R_3N/RX}$. The solvent effect on values of $\Delta G^\ddagger$ for the organometallic reactions (Table 7B and C) is intermediate in magnitude between that on the S_N1 reaction and that on the S_N2 reaction (Table 7D). Whether or not the above qualitative order reflects the polarity of the transition state remains to be seen; possibly, a dissection of solvent effects into initial-state and transition-state contributions would be of help, and we are currently engaged on this problem.

TABLE 7

The effect of alcoholic solvents on $\Delta G^\ddagger$ values (kcal mol^{-1}) for some substitution reactions [a]

	Reactants	T/K	MeOH	EtOH	Pr^{n}OH	Pr^{i}OH	Bu^{n}OH	Bu^{t}OH	Ref.
A	Solvolyses								
	$\mathrm{Ph_2CHCl}$	298	0	1·62		2·95			*b*
	$\mathrm{Bu^tCl}$	298	0	1·32	1·68	2·24	1·94	2·96	5
	$\mathrm{Bu^tBr}$	298	0	1·21		2·10		2·78	5
	$\mathrm{PhCH_2Br}$	338	0	0·50	0·77	1·54 [c]	1·09		22
B	Iododemetallations								
	$\mathrm{Me_4Sn + I_3}$	298	0	1·19	1·99	1·96			This work
	$\mathrm{Et_4Sn + I_2}$	298	0	1·14	1·89	1·56			This work
	$\mathrm{Me_4Pb + I_2}$	298	0	0·99	1·46				5, 16
	$\mathrm{Et_4Pb + I_2}$	298	0	0·87	1·37				5, 16
C	S_E2 reactions with mercury(II) salts								
	$\mathrm{Me_4Sn + HgI_2}$	298	0	0·63	1·06		1·32	2·74	This work
	$\mathrm{Et_4Sn + HgI_2}$	298	0	0·79	1·20		1·51	3·10	This work
	$\mathrm{Me_4Sn + HgCl_2}$	298	0	0·57	0·83		1·12	2·11	This work
	$\mathrm{Et_4Sn + HgCl_2}$	298	0	0·80	1·10		1·34	2·50	This work
	$\mathrm{Et_4Sn + Hg(OAc)_2}$	298	0	0·61	0·79		0·98	2·94	This work
D	S_N2 Menschutkin reactions								
	$\mathrm{Py + C_{12}H_{25}Br}$	348	0	0·54	0·91	1·08	1·12	1·60	23
	$\mathrm{Me_3N + ArCH_2Cl}$	298	0	0·60	0·90				24
	$\mathrm{Py + EtI}$	298	0	0·56	0·84	0·88	0·96	1·09	25
	$\mathrm{PhCH_2NMe_2 + MeI}$	303	0	0·45		0·81			26
	$\mathrm{Et_3N + EtBr}$	339	0	0·41	0·70				27
	$\mathrm{Pr^n{}_3N + MeI}$	293	0	0·39	0·69	0·69	1·08	0·49	11, This work
	$\mathrm{Et_3N + EtI}$	298	0	0·32	0·65	0·49	0·90	0·41	This work
	$\mathrm{PhCH_2NEt_2 + MeI}$	303	0	0·20	0·65		0·89		28

[a] Values of $\Delta G^\ddagger$ calculated from second-order rate constants (sections B—D) are expressed on the mol-fraction scale. [b] E. D. Hughes, C. K. Ingold, and N. A. Taher, *J. Chem. Soc.*, 1940, 949; S. Altscher, R. Baltzly, and S. W. Blackman, *J. Amer. Chem. Soc.*, 1952, **74**, 3649; S. Winstein, A. H. Fainberg, and E. Grunwald, *J. Amer. Chem. Soc.*, 1957, **79**, 4146. [c] A value of 1·51 kcal mol^{-1} at 303 K can be calculated from rate constants given by Y. Kondo, M. Ohnishi, and N. Tokura, *Bull. Chem. Soc. Japan*, 1972, **45**, 3579.

By comparison with the effect of the primary alcohols, the branched-chain alcohols Pr^{i}OH and Bu^{t}OH give rise to a number of anomalous effects. If the solvolyses reactions (Table 7A) are arbitrarily taken as a reference base, then the branched-chain alcohols tend to result in an increase in $\Delta G^\ddagger$ values for the organometallic reaction (3) but to decrease $\Delta G^\ddagger$ values for the iododemetallation reaction (4) and for the Menschutkin reaction. The effect is so marked in the latter case [*] that values of $\Delta G^\ddagger$ in Bu^{t}OH can be even lower in value than $\Delta G^\ddagger$ in the alcohols Pr^{n}OH and Bu^{n}OH. Here again, initial-state and transition-state contributions might be needed for further progress to be made.

EXPERIMENTAL

Alcohols were dried over freshly ignited calcium oxide or calcium sulphate and then distilled. Triethylamine and tri-n-propylamine were stored over sodium hydroxide pellets, filtered, and distilled. Alkyl iodides were allowed to stand over anhydrous sodium carbonate and anhydrous sodium sulphate, filtered, distilled, and stored in the dark. The tetra-alkyltins were prepared and purified as before.[29,30] Mercury(II) chloride and iodide were recrystallised three times from methanol, and dried at 338 K *in vacuo* for several hours; mercury(II) acetate was recrystallised twice from glacial acetic acid.

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[*] It is interesting that the effect of the alcohols Pr^{i}OH and Bu^{t}OH on the pyridine–dodecyl bromide reaction appears to be quite normal, but this reaction was carried out at 348 K.

[23] K. Murai and C. Kimura, *Nippon Nogei-Kagaku Kaishi*, 1972, 2209.

[24] H. von Halban, *Z. phys. Chem.*, 1913, **84**, 129; M. H. Abraham, *J. Chem. Soc.* (*B*), 1971, 299.

[25] J. F. Norris and S. W. Prentiss, *J. Amer. Chem. Soc.*, 1928, **50**, 3042.

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[27] A. von Hemptinne and A. Bekaert, *Z. phys. Chem.*, 1899, **28**, 225.

[28] K. Mukherjee, J. N. Kar, G. B. Behera, R. C. Acharga, and M. K. Rout, *Indian J. Chem.*, 1971, **9**, 947.

[29] M. H. Abraham and T. R. Spalding, *J. Chem. Soc.* (*A*), 1968, 2530; 1969, 399.

[30] M. H. Abraham and G. F. Johnston, *J. Chem. Soc.* (*A*), 1970, 188, 193.

The Menschutkin Reaction.—Rate constants for the triethylamine–ethyl iodide reaction at 298·15 ± 0·01 K were obtained as follows. Solutions of the reactants, after thermostatting, were mixed to give a reactant solution equimolar in triethylamine and ethyl iodide. Aliquot portions (1 or 2 ml) were removed from the reactant solution periodically, added to ice-cold water, and the resulting aqueous alcoholic solution titrated against 0·05M-nitric acid using a 10 ml microburette calibrated to 0·02 ml, with Methyl Red indicator. The simplified kinetic equation (5) was used, and excellent straight lines obtained; runs were followed for up to 100 h and resulted in conversions of 20—30%. About 8—10 kinetic runs were carried out in each solvent with initial concentration (a) varied between 0·1 and 0·4M; no variation in rate constant with initial

$$kt = 1/(a - x) - 1/a \qquad (5)$$

concentration of reactants was noted, and the average values of the rate constants together with their percentage variances are in Table 1. Except in the case of solvent methanol, the product salt $Et_4N^+I^-$ precipitated out during the course of the kinetic run, but this appeared to have no effect on the calculated value of the rate constant.

TABLE 8

Rate constants for the reaction of tetra-alkyltins with mercury(II) salts at 298·15 ± 0·01 K

Reactants	Solvent	Initial concentration (10^3M)		No. of runs	k [a]	v(%) [b]
		R_4Sn	HgX_2			
$Me_4Sn + HgCl_2$	EtOH	10·0	5·0	6	50·85	1·1
$Me_4Sn + HgI_2$	EtOH	10·0	5·0	6	9·26	2·9
$Et_4Sn + HgCl_2$	EtOH	22·0	12·0	6	0·0745	1·0
$Et_4Sn + HgI_2$	EtOH	20·0	13·0	5	0·0581	1·1
$Et_4Sn + Hg(OAc)_2$ [c]	EtOH	9·0	4·0	8	14·29	3·1
$Me_4Sn + HgCl_2$	Pr^nOH	6·0	4·0	6	42·52	1·1
$Me_4Sn + HgI_2$	Pr^nOH	11·0	4·0	6	5·65	0·7
$Et_4Sn + HgCl_2$	Pr^nOH	18·0	6·1	4	0·0594	0·7
$Et_4Sn + HgI_2$	Pr^nOH	30·0	10·0	5	0·0369	3·0
$Et_4Sn + Hg(OAc)_2$ [c]	Pr^nOH	5·0	2·8	7	13·66	4·3
$Me_4Sn + HgCl_2$	Bu^nOH	6·0	4·0	6	31·72	1·5
$Me_4Sn + HgI_2$	Bu^nOH	11·0	4·5	7	4·49	2·5
$Et_4Sn + HgCl_2$	Bu^nOH	11·0	5·7	6	0·0471	3·3
$Et_4Sn + HgI_2$	Bu^nOH	15·0	6·0	5	0·0272	4·8
$Et_4Sn + Hg(OAc)_2$ [c]	Bu^nOH	5·8	3·6	6	12·10	3·6

[a] In l mol^{-1} min^{-1}. [b] Percentage variance in the rate constant. [c] Runs carried out in presence of acetic acid ($3{\cdot}5 \times 10^{-2}$M).

The tri-n-propylamine–methyl iodide reaction was followed by a similar procedure. In this case, the rate constants calculated through equation (5) increased with time, and the values given in Table 1 refer to initial rates of reaction.

The R_4Sn–HgX_2 *Reactions.*—These reactions in the alcohols EtOH, Pr^nOH, and Bu^nOH were set up and followed exactly as described before, using the calibrations originally determined by Abraham and Johnston.[30] Using the normal second-order equation, excellent straight lines were obtained, and runs were followed to at least 50% reaction. Details of the runs are given in Table 8.

Iododemetallations.—When sufficient iodide ion is present to convert essentially all iodine into the I_3^- ion, the iododemetallation of tetra-alkyltins in polar solvents follows[17] the rate equation (6) where the observed second-order rate constant, k_2^{obs}, is related to the actual second-order rate constant, k_2, by the expression $k_2 = k_2^{obs}K[I^-]$. Here K

$$d[I_3^-]/dt = k_2^{obs}[R_4Sn][I_3^-] \qquad (6)$$

is the equilibrium constant for formation of I_3^- and $[I^-]$ the concentration of iodide ion. In the present work, runs were set up not only with an excess of iodide ion over iodine but also with an excess of tetra-alkyltin. Hence, from equation (6), $k_1^{obs} = k_2^{obs}[R_4Sn]$ where k_1^{obs} is the observed first-order rate constant for loss of I_3^-, and the actual second-order rate constant is given by equation (7).

$$k_2 = k_1^{obs}K[I^-]/[R_4Sn] \qquad (7)$$

A solution containing the appropriate concentration of tetra-alkyltin and tetra-n-butylammonium iodide was placed in the sample and reference cells (1 cm) in an SP 500 spectrophotometer equipped with a cell-housing thermostatted at 298·15 ± 0·2 K. After equilibration, *ca.* 7 μl of a solution of iodine in the solvent was added to the sample cell, either *via* a hypodermic syringe or, for fast reactions, *via* a rapid-mixing device designed by Dr. G. Buist. The optical density due to I_3^- at 290 nm was automatically monitored by an on-site computer, programmed to plot out the first-order slope obtained by Guggenheim's method. A number of successive additions of iodine were made to the same sample cell, but normally there was no variation of the observed first-order constant with these additions. The calculated actual second-order rate constants, together with their percentage variances, are in Table 5, and refer to results from 5—8 kinetic runs in each case. The only difficulty encountered was in the case of iododemetallation of tetraethyltin in propan-2-ol where successive additions of iodine resulted in marked increases in the observed first-order constants. Although over 20 kinetic runs were carried out (some calculated by Guggenheim's method and some by the normal first-order equation), only an approximate value for the rate constant was obtained in this case.

In separate experiments it was ascertained that solutions of iodine in the various alcohols in the presence of 10^{-3}M-Bu^n_4NI (*i.e.* under the exact kinetic conditions) were stable over the times during which the runs were monitored.

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