Redox Transfer. Part VIII.[1] Addition of Benzenesulphonyl Chloride and Carbon Tetrachloride to Substituted Styrenes: a Kinetic Study

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A kinetic study of the copper chloride-catalysed addition of benzenesulphonyl chloride to a number of styrenes carrying substituents of widely different electronegativity shows that the overall rates are very little affected by the substituent. This rules out the possibility of a concerted reaction, in which the olefin should participate in the rate-determining step. and confirms a redox chain mechanism. The lack of stereospecificity of the addition of carbon tetrachloride to norbornene points to the same conclusion. β-Methylstyrene reacts much more slowly with benzenesulphonyl chloride than the other styrenes. This is attributed to an unfavourable equilibrium for sulphonyl radical addition to this olefin. Carbon tetrachloride adds at the same rate to different olefins, including β-methylstyrene. in accord with the redox chain mechanism.

THE mechanism which should explain the copper chloride-catalysed formation of 1 : 1 adducts from vinylic monomers and chlorine-containing substrates such as carbon tetrachloride,[2] chloroform,[3] sulphonyl chlorides[4] or derivatives of di- and tri-chloroacetic acid,[5] depends on the presence of cupric chloride (an extremely efficient radical scavenger) in sufficient concentration to suppress telomerization [step (4)].

diazonium chlorides with olefins,[7] and for other redox transfer reactions.[8]

Although the lack of stereospecificity in the redox transfer addition of carbon tetrachloride to but-2-ene was cited [2] as evidence against such a process, it was deemed desirable to investigate this point more thoroughly. This was done by a kinetic study of the addition of carbon tetrachloride and benzenesulphonyl
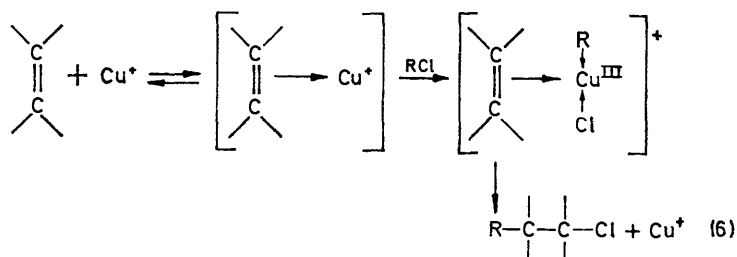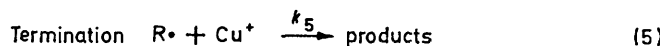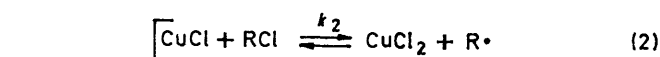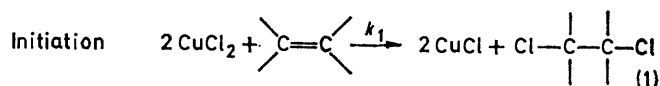
Since the concentration of copper(II) chloride (or the chlorocuprates generally used) during the addition is often quite low, an alternative, concerted reaction mechanism (6) could not be ruled out.[6]

A similar mechanism was suggested for the Meerwein reaction, i.e. the copper chloride-catalysed reaction of

chloride to various substituted styrenes, and by re-examining the stereochemistry of the addition to a rigid olefin, norbornene, which does not allow rotation after addition of a radical.

EXPERIMENTAL

Acetonitrile and carbon tetrachloride were Fluka puriss., and 2,3-dimethylbutadiene was Fluka pract. β-Methyl-,

[1] J. Sinnreich and M. Asscher, *J.C.S. Perkin I*, 1972, 1543.
[2] M. Asscher and D. Vofsi, *J. Chem. Soc.*, 1963, 1887.
[3] M. Asscher and D. Vofsi, *J. Chem. Soc.*, 1963, 3921.
[4] M. Asscher and D. Vofsi, *J. Chem. Soc.*, 1964, 4962.
[5] S. Murai, N. Sonoda, and S. Tsutsumi, *J. Org. Chem.*, 1964, **29,** 2104; S. Murai and S. Tsutsumi, *ibid.*, 1966, **31,** 3000.

[6] A. Orochov, M. Asscher, and D. Vofsi, *J. Chem. Soc. (B),* 1969, 255.
[7] G. N. Schrauzer, *Chem. Ber.*, 1961, **94,** 1891.
[8] V. L. Zvezdin, G. A. Domrachev, Yu. A. Sangalov, and Yu. D. Semchikov, *Doklady Akad. S.S.S.R.*, 1971, **198,** 102.

p-methyl, *p*-chloro, *m*-chloro, and *m*-nitrostyrene, and norbornene were all Aldrich pure. Styrene was B.D.H. analytical. Cupric chloride and triethyl ammonium chloride were as in ref. 4. Benzenesulphonyl chloride was freshly distilled before use, b.p. 120 °C at 15 mmHg.

The rate studies were carried out by dilatometry as described in ref. 6.

The rates of addition of benzenesulphonyl chloride to the various styrenes were measured at 110 °C in acetonitrile, with the following concentrations: 1M-styrene, 0·5M-sulphonyl chloride, 2mM-cupric chloride, and 3mM-triethylammonium chloride. For additions of carbon tetrachloride, the concentrations were: 1M-olefin, 0·5M-carbon tetrachloride, 5mM-cupric chloride, and 7·5mM-triethylammonium chloride.

RESULTS AND DISCUSSION

Rate-determining Step.—Under conditions such that nearly all the copper chloride is kept in the Cu^I form during the reaction, the rate-determining step in the chain mechanism is the oxidation of cuprous chloride by the chlorinated substrate RCl,[6] where R stands for CCl_3, $CHCl_2$, or RSO_2 [step (2)]. The overall rate of addition should then be independent of the nature of the olefin. The concerted mechanism, on the other hand, requires such a dependence, again assuming that the oxidation of the Cu^I olefin complex by RCl in step (6) is rate-determining. Even if this is not the case, the rate of formation and decomposition of the hypothetical complex (between brackets) into the products should be affected by the nature of the olefin.

Addition of Benzenesulphonyl Chloride to Substituted Styrenes.—In an earlier study,[6] substituted arylsulphonyl chlorides were added to styrene under conditions which assured a constant Cu^I level. The addition was found to be first order, both in copper chloride and in sulphonyl chloride, and closely obeyed the Hammett equation. In the present work, the reaction of benzenesulphonyl chloride with substituted styrenes was examined under the same conditions. Substituents of widely varying electronegativity appeared to affect the overall rate of addition only slightly (see Table 1), with no apparent correlation with Hammett values. These styrenes can be expected to co-ordinate with cuprous ion to a vastly different extent, thus affecting the rate of step (6), if this were to be rate determining. Furthermore, *p*-methylstyrene co-ordinated with cuprous chloride should react faster with sulphonyl chloride than a similar complex with *m*-nitrostyrene on account of the greater reducing power of the former. The absence of a clear substituent effect indicates that other factors govern the overall rate of addition.

Behaviour of β-Methylstyrene.—β-Methylstyrene showed an exceptionally low rate of addition (4·4 × 10⁻³ compared to 8·2 × 10⁻² l mol⁻¹ s⁻¹ for styrene). This indicates that, under our conditions, step (2) is no longer rate-determining. The complication is most probably introduced by the high degree of reversibility of step (3). Even for styrene, this step is appreciably reversible, as demonstrated by its inability to inhibit the sulphonyl radical sensitized *cis–trans* isomerization

of but-2-ene.[1,4] In comparison with styrene, the equilibrium for sulphonyl radical addition to β-methylstyrene, $RSO_2\cdot + MeCH{:}CHPh \rightleftharpoons MeCH(RSO_2)\dot{C}HPh$, will be much displaced to the left, for the addition

TABLE 1

First-order rate constants for the addition of benzenesulphonyl chloride to substituted styrenes in acetonitrile at 110 °C

R	Hammett σ value [a]	$10^{-2}k/min^{-1}$
p-Me	−0·17	1·25
H	0	1·15
p-Cl	0·23	1·20
m-Cl	0·37	1·25
m-NO₂	0·71	1·00

[Styrene] = 1M; [benzenesulphonyl chloride] = 0·5M; [CuCl₂] = 2 × 10⁻³M; [triethylammonium chloride] = 3 × 10⁻³M

[a] Taken from C. D. Ritchie and W. F. Sager, *Progr. Phys. Org. Chem.*, 1964, **2**, 334.

of any radical, and particularly the bulky sulphonyl radical, is hindered by the β-methyl group. [Compare the trichloromethyl affinity of styrene (100) relative to that of β-methylstyrene (1·1).[9]]

The reaction is still close to first order in sulphonyl chloride. This result is still consistent with the general rate expression (7) derived earlier [6] which can be written

$$d(RCl)/dt = -k_2(RCl)(CuCl)$$

$$\left[1 - \cfrac{1}{1 + \cfrac{k_3(\text{olefin})}{k_{-2}(CuCl_2)}\left(1 - \cfrac{k_{-3}}{k_{-3} + k_4(CuCl_2)}\right) + \cfrac{k_5(CuCl)}{k_{-2}(CuCl_2)}}\right] \quad (7)$$

as (8) where *f* is given by equation (9).

$$d(RCl)/dt = -k_2(RCl)(CuCl)/(1 + f) \quad (8)$$

$$f = \cfrac{k_{-2}}{\cfrac{k_3 k_4(\text{olefin})}{k_{-3} + k_4(CuCl_2)} + k_5 \cfrac{(CuCl)}{(CuCl_2)}} \quad (9)$$

Expression (9) may be written in the form $f = a/(bx + c)$. Under conditions such that *b* is relatively small compared to *c*, *f* becomes practically independent of *x* (while *x* changes between the limits of 0·5—1·0M under our experimental conditions). Since *b* will be largely governed by the relative magnitude of k_{-3} and k_3, the extent of reversibility of step (3) may thus greatly influence the value of the overall rate constant, without much upsetting the first-order dependence on the sulphonyl chloride concentration. This was borne out by our dilatometric measurements for all the investigated styrenes, including β-methylstyrene.

Carbon Tetrachloride Additions.—In contrast to sulphonyl radicals, trichloromethyl radical addition to olefins is irreversible, and if the redox transfer chain mechanism is operative, with step (2) rate determining, carbon tetrachloride should add to all olefins at the same rate. This was confirmed for four widely different olefins

[9] C. Walling, 'Free Radicals in Solution,' Wiley, New York, 1957, p. 254.

(Table 2) which clearly shows that the olefin has no role in the rate-determining step.

TABLE 2

Second-order rate constants for the addition of carbon tetrachloride to olefins in acetonitrile at 110 °C

Olefin	$10^3 k_2/\text{l mol}^{-1}\text{ s}^{-1}$
(1) Styrene	4·2
(2) β-Methylstyrene	3·7
(3) Dimethylbutadiene	4·5
(4) Norbornene	4·1

[Copper chloride] $= 5 \times 10^{-3}\text{M}$; [triethylammonium chloride] $= 7\cdot5 \times 10^{-3}\text{M}$; [CCl$_4$] $= 0\cdot5\text{M}$; [olefin] $= 1\text{M}$.

Measured in this way, the second-order rate constant for the oxidation of cuprous chloride by carbon tetrachloride is $4\cdot2 \times 10^{-3}$ l mol^{-1} s^{-1} at 110 °C (cf. an earlier rough estimate:[10] 5×10^{-6} l mol^{-1} s^{-1} at 22 °C).

* Dickerman et al.[11] have reached the same conclusion for the Meerwein reaction.

Non-stereospecificity of Carbon Tetrachloride Additions.—The addition product of carbon tetrachloride to a rigid olefin like norbornene was examined in reactions which were catalysed either by peroxide or by copper chloride. In the first case, there can be no doubt about the two stages of the reaction: addition of a radical, followed by displacement on carbon tetrachloride. A truly concerted reaction, taking place within the complex depicted in (6), should lead to exclusive *cis*-addition. In fact, in both cases, identical mixtures of stereoisomers were obtained.

In summary, while olefin–Cu$^\text{I}$ complexes are well documented in the literature, we have found no proof for their participation in the redox transfer reaction.*

[10] M. Asscher and D. Vofsi, *J. Chem. Soc. (B),* 1968, 947.
[11] S. C. Dickerman, D. J. De Souza, and N. Jacobson, *J. Org. Chem.,* 1969, **34**, 710.