

REACTIVITY OF SUBSTITUTED STYRENES IN THE CATALYTIC ADDITION REACTION WITH THE TRICHLOROMETHYL RADICAL

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Relative reactivities have been investigated in the catalytic addition of tetrachloromethane to substituted styrenes by the competitive method. The polar effects of substituents on benzene ring were correlated with Hammett equation for a copper and ruthenium catalyst, giving ρ values equal to -0.39 and -0.18 respectively. The results indicate that in contrast to classical additions the catalytic addition of tetrachloromethane is not a free radical chain process but that the trichloromethyl radical, presumably coordinated, reacts with the carbon-carbon double bond via innersphere pathways.

The study of polar effects in addition reactions is very attractive from theoretical and mechanistic point of view. Linear Free Energy Relationship (LFER) of Hammett type is thus a very useful tool for the elucidation of reaction mechanism of both heterolytic and homolytic reactions. The substituent effects of styrene have not been investigated systematically in homolytic addition reactions, probably because of certain anomalies¹. Nevertheless, substituted styrenes or α -methylstyrenes have been found as convenient model compounds for the study of polar effects in addition reactions with free radicals of different polarity.

Reported data showed that polar effects in homolytic additions are much smaller than in ionic additions^{2,3}. In addition to copolymerization¹, also correlation data on addition of trichloromethyl^{4,5}, alkyl⁶, phenylalkyl⁷⁻⁹ radicals or sulphur¹⁰⁻¹² and nitrogen-^{13,14} centered radicals have been published. All the addition reactions studied proceeded via classical free radical chain mechanism and were initiated by conventional methods like organic peroxides^{5,4,7}, azo compounds^{8,9}, organometallics^{6,13} or photo technique^{10-12,14}. In the case of the benzenesulfonyl radical generated by the redox system $\text{Cu}^{\text{I}}/\text{Cu}^{\text{II}}$, the Hammett correlation failed because of the high degree of reversibility of the addition of benzenesulfonyl chloride to substituted styrenes under the conditions used¹⁵.

As a part of our research program directed toward elucidation of reaction mechanisms by means of structure-reactivity relationships, we have decided to investigate the relative reactivities of substituted styrenes toward the trichloromethyl radical

generated from tetrachloromethane. The conventional methods of initiation (org. peroxides, azo compounds etc.) has prevented to use the addition of tetrachloromethane to styrenes as a model reaction for polar effect studies, because of preferential polymerization of styrenes. In our study we used metal complexes acting as very selective catalysts.

EXPERIMENTAL

Materials. Tetrachloromethane (Lachema Brno), diethylamine (Laborchemie, Apolda), styrene (Kaučuk, Kralupy) 4-methylstyrene, 4-fluorostyrene, 4-chlorostyrene, 4-bromostyrene (all Fluka AG, Buchs). Styrenes were distilled under reduced pressure before use and stored under nitrogen in a refrigerator. 3-Nitrostyrene was prepared by reported procedure¹⁶. Cuprous chloride was purified as reported¹⁷. Tris(triphenylphosphine)rutheniumchloride (Fluka AG Buchs) was used as obtained.

Analytical methods. GC analysis of products and reaction mixtures were carried out on Chrom 41 instrument equipped with FID detector, CI 100 integrator (Laboratorní přístroje, Prague) and glass column (1.2 m × 3 mm) packed with 3% Silicone OV-17 on Gas-Chrom Q. ¹H NMR and ¹³C NMR spectra of the products were recorded on Varian XL 200 spectrometer.

Preparation of 1 : 1 adducts. A mixture of tetrachloromethane, a substituted styrene (10 mmol), cuprous chloride and diethylamine in molar ratio 10 : 1 : 0.02 : 0.04 was magnetically stirred and heated to reflux (76°C) under nitrogen for 2–4.5 hours. The product (1 : 1 adduct) was isolated by distillation under reduced pressure. The products are new compounds and their data are given in Table I. They were identified by ¹H and ¹³C NMR analysis.

Competitive kinetic runs. Tetrachloromethane, styrene (2.6 mmol), substituted styrene (2.6 mmol) and catalyst in molar ratio 40 : 1 : 1 : 0.02 were accurately weighed into a flask with an internal standard (hexadecane). Copper catalyst, Cu(Et₂NH)₂Cl, was prepared in situ from cuprous chloride and diethylamine in the ratio 1 : 2. Ruthenium catalyst Ru(PPh₃)₃Cl₂ was used in 0.005 molar ratio to styrene. The reaction mixture were then magnetically stirred and heated to reflux (76°C) under nitrogen. Each ten minutes the samples of reaction mixture were analyzed after cooling by GC to determine styrene conversion (up to 30–50%). The relative rates were followed by the formation of 1 : 1 adducts and determined by calibration with authentic

TABLE I
1 : 1 Adducts obtained (XC₆H₄CHClCH₂CCl₃)

X	B.p., °C/Pa	Yield, %	Calculated/Found	
			% C	% H
4-CH ₃	96/67	86.5	44.16/44.10	3.71/3.65
4-F	103/67	85.5	39.17/39.11	2.56/2.52
4-Cl	116/93	84.9	36.97/36.93	2.41/2.42
4-Br	129/93	77.7	32.09/32.24	2.10/2.16
3-NO ₂	146/53	59.7	35.68/35.68	2.33/2.35

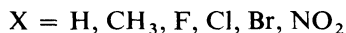
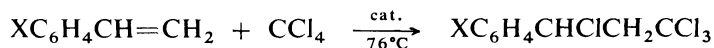
samples. The competitive experiments with a couple of styrenes were repeated at least three times and the average values of relative rate constants were calculated. The relative rate constants (k_X/k_H) were calculated from the usual expression:

$$k_X/k_H = \ln(1 - x_X)/\ln(1 - x_H),$$

where x_X is the conversion of a substituted styrene and x_H is the conversion of styrene.

RESULTS AND DISCUSSION

In most kinetic studies⁴⁻¹⁴ the disappearance of olefins was followed to determine relative rate constants. This method can be used provided that the reactant is consumed by the reaction claimed by the author as being studied. However, this condition need not be fulfilled in all cases¹². In our model system we used the method based on formation of the products (1 : 1 adducts), which provides experimental data with higher accuracy.



The side reactions which would complicate the situation like telomerization or polymerization were disregarded on the ground of the high selectivity of the catalytic systems used in this study. The only exception concerned 4-methoxystyrene where the high degree of polymerization prevented us to obtain a reliable value of the rate of addition. Tendency of this monomer toward spontaneous polymerization was observed previously also in the addition reactions with bromotrichloromethane⁴ and 4-toluenesulfonyl iodide¹².

For the present kinetic investigation we chose the competitive reaction of substituted and unsubstituted styrene with tetrachloromethane in the presence of copper or ruthenium catalyst. Relative rate constants determined for $\text{Cu}(\text{Et}_2\text{NH})_2\text{Cl}$ and $\text{Ru}(\text{PPh}_3)_3\text{Cl}_2$ catalysts are presented in Table II. The relative rate constants (k_X/k_H) were correlated with Hammett σ constants:

$$\log(k_X/k_H) = \rho\sigma.$$

No significant differences were observed when Hammett-Brown σ^+ constants were employed for the correlation, as demonstrated by close values of the correlation coefficients (0.9995 and 0.9926 resp.). However, anomaly was found for substituent H (styrene) in Hammett treatment of the reactivity data for both catalysts. As follows from the correlation coefficients when H-substituent is excluded, the value rises from 0.9479 to 0.9995 for the copper catalyst and from 0.9179 to 0.9988 for the ruthenium catalyst. The deviation of H-substituent in the correlation is evident

from Fig. 1. This anomaly which was further confirmed by cross-competitive experiments using 4-methylstyrene instead of styrene as a standard, is difficult to explain. A similar situation in the addition of 4-toluenesulfonyl radical to substituted styrenes was already reported¹². When H-substituent is excluded, the correlation coefficient in that study changes from 0.938 to 0.9970. The authors¹² did not comment this phenomenon.

The magnitude of ρ constants indicates a modest dependence of the reaction upon substituent effects in the system for both copper and ruthenium catalyst. The negative ρ values found in this study agree with electrophilic nature of the trichloromethyl radical observed also in other studies^{4,5}. Different ρ values for the copper and ruthenium catalyst suggest that the catalyst contributes via central metal atom (or ligand

TABLE II
Relative reactivities of substituted styrenes ($\text{XC}_6\text{H}_4\text{CH}=\text{CH}_2$) toward trichloromethyl radical for copper and ruthenium catalyst

X	k_X/k_H		σ^a
	Cu-cat.	Ru-cat.	
4-CH ₃	1.44 ± 0.02	1.22 ± 0.03	-0.17
H	1.00	1.00	0.00
4-F	1.16 ± 0.01	1.09 ± 0.02	0.06
4-Cl	0.99 ± 0.02	1.03 ± 0.02	0.23
4-Br	1.02 ± 0.07	1.03 ± 0.05	0.23
3-NO ₂	0.65 ± 0.04	0.84 ± 0.02	0.71

^a Ref.¹⁸.

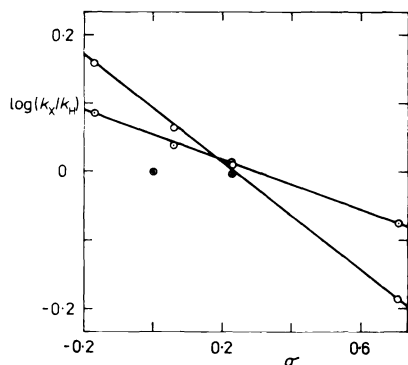
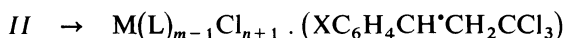
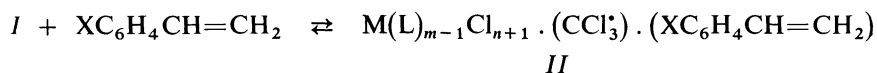
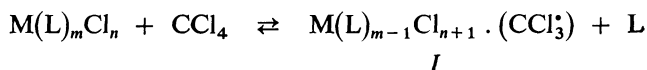


FIG. 1
Correlation of $\log(k_X/k_H)$ and Hammett constant σ for the addition of tetrachloromethane to substituted styrenes catalyzed by copper (○) and ruthenium (◐) complexes

respectively), to an intermediate structure in the transition state, though it is not clear whether the electrophilic trichloromethyl radical can form a complex with the catalyst. (Our effort to detect the presence of intermediate complex between reactants and catalyst by EPR and UV spectroscopy has not been successful). Nevertheless, we suggest formation of the complexed trichloromethyl radical both with copper and ruthenium complexes as catalysts. We believe that the trichloromethyl radical is complexed in a reversible step prior to the addition to the carbon-carbon double bond (presumably coordinated) and the addition reaction take place via innersphere pathway (Scheme 1).



SCHEME 1

The proposed mechanism of catalytic addition reactions differs from the chain mechanism of classically initiated or redox-catalyzed reactions. We believe that copper and ruthenium complexes catalyze these addition reactions via non-chain process. The similar consideration on the mechanism of addition of polyhaloalkanes to alkenes in the presence of copper and ruthenium complexes have been recently reported¹⁹⁻²¹. This work is the first example of catalytic study of polar effects in addition reactions using Hammett-type linear free-energy treatment. It proved to be useful tool for determining not only the electronic character of attacking radical species, but also for getting a deeper insight into reaction mechanism. Therefore, it is of interest to compare our results with the previous non-catalytic studies⁴⁻¹⁴ performed by initiation technique under free radical conditions.

The ρ values obtained in additions of the trichloromethyl radical (conventionally generated from bromotrichloromethane) to substituted styrenes⁴ amounted to -0.42 and to substituted α -methylstyrenes⁵ to -0.7 . Absolute values of ρ constant for substituted α -methylstyrenes are somewhat higher than for substituted styrenes (Table III). The study of the addition of trichloromethyl radical to substituted 3-phenyl-1-propenes and 4-phenyl-1-butenes, where carbon-carbon double bond is insulated from the phenyl group by one or two methylene groups, has led to ρ values -0.29 and -0.20 , although lower ρ values were expected²². As summarized in Table III, in all cases the ρ values are negative, in accordance with the expected electrophilic nature of trichloromethyl radical. Its magnitude variation can be influenced not only by olefinic substrate, but also by complexation with transition

metal complexes, as resulted from our study. It is generally accepted that the magnitude of Hammett ρ constant reflexes the electronic nature of attacking radical species to carbon-carbon double bond. This statement was confirmed in our laboratory by theoretical study of electronic nature of free radicals in the addition to substituted styrenes varying from electropositive to electronegative nature²³. Some additional ρ and ρ^+ values obtained in other free radical additional reactions with substituted styrenes and α -methylstyrenes are presented in Table III. Although paucity of the data does not allow systematic discussion of polar effects and regardless of the fact that certain data were correlated by Hammett-Brown equation (ρ^+), some important observations can be mentioned.

The electrophilic nature exhibit besides trichloromethyl radical also styrenylperoxy, 4-methoxystyrenylperoxy, benzenethiyl, 4-chlorobenzenethiyl, 4-toluenesulfonyl and

TABLE III
The ρ and ρ^+ values for addition reactions of some radicals with substituted styrenes and α -methylstyrenes

Reaction	Generation	Temp., °C	ρ	ρ^+	Ref.
$\text{CCl}_3\cdot$	Cu-cat.	76	-0.39	—	this work
$\text{CCl}_3\cdot$	Ru-cat.	76	-0.18	—	this work
$\text{CCl}_3\cdot$	DBP ^a	80	-0.42	-0.42	4
$\text{CCl}_3\cdot$	DTBP ^b	105	-0.70 ^c	—	5
$\text{C}(\text{CH}_3)_3\cdot$	R-HgX	-20	1.10	—	6
$\text{C}_6\text{H}_{11}\cdot$	R-HgX	-20	0.68	—	6
$\text{C}_6\text{H}_{13}\cdot$	R-HgX	-20	0.45	—	6
$\text{C}_6\text{H}_5\text{CHCH}_2\cdot$	DBP ^a	60	0.51	—	7
$\text{C}_6\text{H}_5\text{CHCH}_2\cdot$	AIBN ^d	30	0.60	—	8
$\text{C}_6\text{H}_5\text{CHCH}_2\text{OOR}\cdot$	AIBN ^d	60	—	-0.30	9
$4\text{-MeOC}_6\text{H}_4\text{CHCH}_2\text{OOR}\cdot$	AIBN ^d	60	-0.40	—	9
$\text{C}_6\text{H}_5\text{S}\cdot$	UV	23	—	-0.26	10
$\text{C}_6\text{H}_5\text{S}\cdot$	UV	23	—	-0.30 ^c	10
$\text{C}_6\text{H}_5\text{S}\cdot$	UV	70	—	-0.38 ^c	11
$4\text{-ClC}_6\text{H}_4\text{S}\cdot$	UV	23	—	-0.56	10
$4\text{-ClC}_6\text{H}_4\text{S}\cdot$	UV	23	—	-0.63 ^c	10
$4\text{-CH}_3\text{C}_6\text{H}_4\text{SO}_2\cdot$	UV	43	-0.55	-0.50	12
$\text{N}(\text{CH}_3)_2\cdot$	TMT ^e	85	0.69 ^c	—	13
$\text{N}(\text{CH}_3)_2\cdot\text{ZnCl}_2$	TMT ^e	85	-0.98 ^c	—	13
$\text{C}_5\text{H}_{10}\text{NH}^+\cdot$	UV	0	-1.34	-1.04	14

^a Dibenzoylperoxide; ^b di-tert-butylperoxide; ^c α -methylstyrenes; ^d azo bis-isobutyronitrile; ^e tetramethyl-2-tetrazene.

piperidinium radicals, while t-butyl, cyclohexyl, n-hexyl, styryl and dimethylamino radicals are nucleophiles. An interesting case of electronic behaviour has been observed in the drastic change of nucleophilic dimethylamino radical ($\rho = 0.69$) into electrophile ($\rho = -0.98$) by its coordination to zinc dichloride¹³. In catalytic additions with copper and ruthenium complexes studied by us we assume that the central metal atom contributes to electronic changes of the trichloromethyl radical via coordination, though in modest extent. One can expect that not only the central metal atom but also attached ligands affect the electronic properties of complexed radicals in transition state. This problem is the subject of further study.

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