

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE UNIVERSITY OF MICHIGAN, ANN ARBOR, MICH.]

A Hammett-Taft Study of the Addition of the Trichloromethyl Radical to Substituted Alkenes

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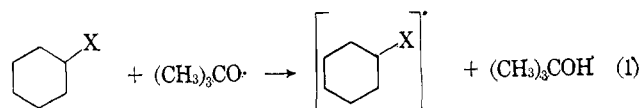
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A Hammett-Taft study of the addition of the trichloromethyl radical to a series of substituted alkenes, $XCH=CH_2$, has led to a ρ^* -value of -0.42 . The ρ^* -values for the addition of the trichloromethyl radical to the double bond in the series $XCH_2CH=CH_2$, $XCH_2CH_2CH=CH_2$, and $XCH_2CH_2CH_2CH=CH_2$ have been found to be -0.15 , -0.06 , and -0.024 , respectively. The interposition of a methylene group between the substituent and the double bond decreases the ρ^* -value by a factor of 2.5.

Introduction

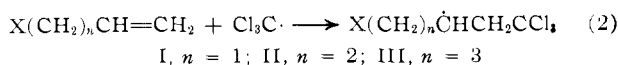
Although free radicals are formally neutral species, it has long been recognized that polar groups in a molecule can have a considerable effect upon the rate and course of homolytic processes. Application of the Hammett equation, $\log k_X/k_0$ vs. $\sigma\rho$, to reactions which produce a free radical containing a substituted phenyl group elsewhere in the molecule has provided a wealth of useful information on the way in which polar groups exert their influence.²⁻¹⁶ Free radical reactions involving purely aliphatic compounds have been the subject of numerous investigations also. It has been found that polar substituents which withdraw electrons by induction tend to decrease the lability of nearby hydrogen atoms toward abstraction by highly reactive radicals such as the chlorine atom.¹⁷⁻²³ Similarly, it has been found that the reactivity of a double bond toward the trichloromethyl radical is reduced when there is present in the molecule a group with an electron-withdrawing inductive effect,²⁴⁻²⁶ provided there is no direct resonance interaction between the reaction center and the polar substituent, in which case reactivity may be increased as a consequence of the stabilizing effect on the radical produced.²⁷⁻³⁰ The first attempt at a quantitative

development of a linear free energy-polar energy relationship, that is a Hammett-Taft plot, applied to a free radical reaction involving only aliphatic compounds, is a recent study of the hydrogen abstraction reaction from a series of polar substituted cyclohexanes by the *t*-butoxy radical (reaction 1).³¹ The ρ^* -value, obtained by plotting $\log k_X/k_0$ vs. the σ^* -value for the



$X-CH_2$ -group, was -0.46 , with a correlation coefficient of -0.84 . If $\log k_X/k_0$ is plotted against the σ^* -value for $X-$, ρ^* is -0.16 . Groups with an electron-withdrawing inductive effect decrease reactivity. The poor correlation is probably a consequence of a lack of constancy of steric and resonance effects within the reaction series. Abstraction of the hydrogen atom α to the substituent produces a radical capable of direct resonance interaction with the substituent. In addition, there are several types of hydrogens capable of being abstracted from the cyclohexane ring, and in some cases additional abstractable hydrogen atoms in the substituent, so that many reactions are actually being studied, and only an average relative reactivity is being measured.

It was the purpose of the work described in this paper to conduct a Hammett-Taft study of a free radical reaction in a series of aliphatic compounds which would not be subject to the above complications. It was desired to study a system in which a single reaction took place to generate a radical carbon atom at a position which precluded direct resonance interactions with the substituent, in a series in which steric effects should approach constancy. For this purpose the addition of the trichloromethyl radical, generated from bromotrichloromethane, to the double bond in series of 1-substituted propenes (I), butenes (II), and pentenes (III) was studied (reaction 2), and the relative reactivity data treated according to the procedure suggested by Taft.³²



Experimental

Materials.—The bromotrichloromethane and chlorobenzene were purified as described elsewhere.¹² *o*-Dichlorobenzene (Eastman) was distilled, b.p. $179-180^\circ$ (lit.³³ 180.4°). It contained small quantities of the *p*-isomer. Allyl alcohol (Eastman) was distilled, b.p. $97-99^\circ$ (lit.³³ 97°). Allyl bromide (Eastman) was distilled, b.p. $70-72^\circ$ (lit.³³ $70-71^\circ$). Allyl cyanide (Aldrich) was distilled, b.p. $116-118^\circ$ (lit.³³ 118°). Allyl methyl ether was prepared by the reaction of allyl bromide and sodium methoxide

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in methanol, b.p. 44–47° (lit.³⁴ 46°). 1-Hydroxy-3-butene (Columbia Organic Chemicals Co.) was distilled, b.p. 113–114° (lit.³⁴ 112.5–113.5°). 1-Bromo-3-butene was prepared from 1-hydroxy-3-butene by the procedure of Linstead and Rydon,³⁵ in 60% yield, b.p. 96–96.5° (lit.³⁵ 97°). 1-Cyano-3-butene was prepared from 1-bromo-3-butene by the procedure of La Forge, Green, and Gersdorff,³⁶ in 61% yield, b.p. 140–142° (lit.³⁶ 140°). 1-Octene (Matheson Coleman and Bell) was distilled, b.p. 121–122° (lit.³⁴ 120–122°). 1-Hydroxy-4-pentene (Columbia Organic Chemicals Co.) was distilled, b.p. 140–142° (lit.³⁴ 140–142°). 1-Bromo-4-pentene was prepared³⁶ from 1-hydroxy-4-pentene in 44% yield, b.p. 126–129° (lit.³⁶ 128–130°). 1-Cyano-4-pentene was prepared³⁶ from 1-bromo-4-pentene in 48% yield, b.p. 164–165° (lit.³⁶ 158–164°). All materials gave a single peak when analyzed by v.p.c. using a 6-ft. 10% diethylene glycol succinate column.

Procedure for Kinetic Runs. Determination of Relative Rates of Addition.—The general procedure was the same as that described elsewhere.¹² Reactant ratios of bromotrichloromethane: alkene(1):alkene(2):chlorobenzene of from 4:4:4:3 to 4:2:2:1, mostly nearer the latter, were employed. The extent of total olefin consumption varied from 10 to 90%. The ratios of rate constants were independent of both reactant ratio and extent of reaction. Reactions were run at 69.5°, with a 275-w. General Electric sunlamp placed 19 cm. from the surface of the constant temperature bath. The agreement between the total number of moles of olefin consumed and the number of moles of bromotrichloromethane consumed was generally within 5%, and the quantity of chloroform produced by hydrogen abstraction by the trichloromethyl radical was so small as to be negligible. These results indicate that there are no side reactions by which the olefins are consumed which significantly compete with addition. Thus, the ratio of rate constants for addition can be calculated from the expression

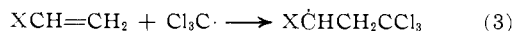
$$\left(\frac{k_1}{k_2}\right) = \frac{\log(\text{moles of 1 initially}/\text{moles of 1 finally})}{\log(\text{moles of 2 initially}/\text{moles of 2 finally})}$$

Analyses were conducted by vapor phase chromatography as described elsewhere.¹²

Calculations.— ρ^* -Values were calculated from least squares slopes of the lines resulting from Hammett-Taft plots of $\log k_X/k_{\text{CH}_2\text{OH}}$ vs. the appropriate σ^* -value. Correlation coefficients were calculated according to standard statistical methods.³⁷

Results and Discussion

The results obtained in these studies can be handled in several ways, each approach emphasizing a different aspect of the polar properties of free radical reactions. According to the original formulation of the Hammett-Taft relationship, the entire group of atoms attached to the reaction center is considered the substituent, and a σ^* -value corresponding to the entire group is used in the calculation of ρ^* . Thus, the reaction under study in this paper becomes the addition of the trichloromethyl radical to a series of substituted ethylenes (reaction 3). In Table I are the relative



reactivity data for all of the compounds studied, taking allyl alcohol (X = CH₂OH) as the reference standard. Propylene (X = CH₃) was not used as a standard, because its physical properties would have required a modification of the procedure used. Allyl alcohol was chosen simply because the σ^* -value for the CH₂OH group is an intermediate one. The change in reference standard will, of course, have no effect on the slope of the regression line, that is on ρ^* , but only the intercept. A graphical plot of $\log k_X/k_{\text{CH}_2\text{OH}}$ vs. σ^* appears in Fig. 1. The data in Table I give a calculated value of σ^* of -0.42 ($r = -0.99$). The excellent correlation of the data by the Hammett-Taft equation implies that the addition of the trichloromethyl radical to the double bond of the series of compounds studied is governed by the inductive polar effect of the substituent, and that steric effects are constant. The nega-

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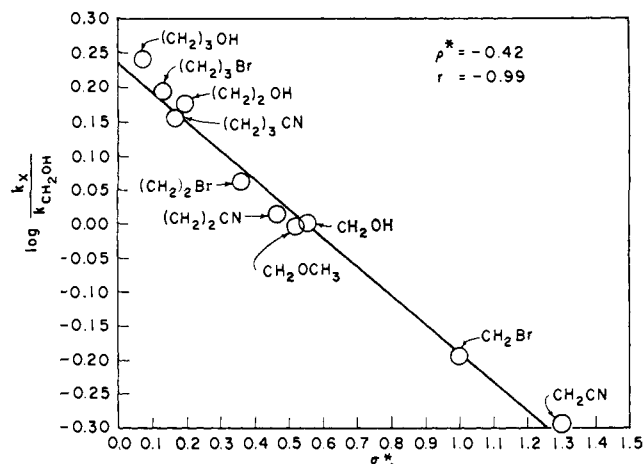


Fig. 1.—Correlation of $\log k_X/k_{\text{CH}_2\text{OH}}$ and σ^* for the addition of $\text{Cl}_3\text{C}\cdot$ to $\text{XCH}=\text{CH}_2$.

tive sign of the ρ^* -value indicates that the reaction is facilitated by factors which increase the electron density at the reaction site and retarded by factors which decrease the electron density at the reaction site. The addition of the trichloromethyl radical to a double bond is a fast, exothermic process. The additions of the trichloromethyl radical to ethylene and propylene have heats of reactions associated with them of -14 and -18 kcal./mole, respectively.^{38,39} The activation

TABLE I

RELATIVE RATES OF ADDITION OF $\text{Cl}_3\text{C}\cdot$ TO $\text{XCH}=\text{CH}_2$ AT 69.5°

X	σ^*	Rel. k
CH ₂ CN	+1.300 ^a	0.51 ± 0.04 ^d
CH ₂ Br	+1.000 ^a	0.64 ± 0.05
CH ₂ OH	+0.555 ^a	1.00
CH ₂ OCH ₃	+ .520 ^a	0.99 ± 0.02
(CH ₂) ₂ CN	+ .464 ^b	1.03 ± .03
(CH ₂) ₂ Br	+ .357 ^b	1.15 ± .10
(CH ₂) ₂ OH	+ .198 ^b	1.51 ± .05
(CH ₂) ₃ CN	+ .166 ^c	1.43 ± .12
(CH ₂) ₃ Br	+ .128 ^c	1.55 ± .15
(CH ₂) ₃ OH	+ .071 ^c	1.75 ± .10

^a Ref. 32, p. 619. ^b $1/2.8 \sigma^*$ for XCH₂ (see ref. 32, p. 592). ^c $1/2.8 \sigma^*$ for X(CH₂)₂. ^d Average deviation.

energy for the addition of the trichloromethyl radical to cyclohexene has been reported to be 3.4 kcal./mole.⁴⁰ These parameters are comparable to those for free radical chlorination of saturated aliphatic hydrocarbons.⁴¹ Thus, it seems safe to classify the reactions studied in this paper as fast, exothermic reactions in which the transition state resembles reactants more closely than products.⁴² Thus the observed polar effects are best interpreted in terms of the effects of substituents on ground state interactions rather than product stability.⁴³ Enhancement of reactivity by inductive electron donation on the part of the substituent must then be a consequence of the resulting higher electron density in the double bond, which facilitates reaction with the electrophilic trichloromethyl radical. Inductive electron removal which decreases the electron density in the double bond

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(43) Other reactions of the trichloromethyl radical, such as hydrogen abstraction, have higher activation energies than addition and are better understood in terms of a transition state resembling products.

results in decreased reactivity. Similar consideration of ground state interactions are used to explain the polar effects operative in the highly exothermic abstraction of a hydrogen atom by the chlorine atom,¹⁷⁻²³ and probably explain the positive Hammett ρ -value observed for the addition of the nucleophilic styryl radical to substituted styrenes.⁴

A slight reshuffling of the data in Table I brings to the fore another very well-behaved feature of the reaction under study. If the substituted propenes (I), butenes (II), and pentenes (III) are considered as separate reaction series, and a ρ^* -value is calculated for the addition of the trichloromethyl radical to the double bond in each series, by plotting $\log k_X/k_{OH}$ vs. σ^* for the group X, then it is possible to observe the effect on ρ^* of the interposition of a methylene group between the reaction site and the polar substituent. This treatment represents a slight modification of the original formulation of the Hammett-Taft relationship, but since the σ^* -value represents the inductive electron-withdrawing power of an atom or group of atoms, the treatment is perfectly valid. In Tables II, III, and IV the pertinent reactivity data are presented, and in Table V the ρ^* -values for the three reaction series are indicated. From the ρ^* -values in Table V it would appear that the interposition of a methylene group between the polar substituent and the double bond decreases the ρ^* -value by a factor of 2.5 ($\rho^*_{n=3} = 1/2.5\rho^*_{n=2}$, $\rho^*_{n=2} = 1/2.5\rho^*_{n=1}$). In the limited number of pertinent classical Hammett studies involving aromatic compounds, it has been found that the interposition of a methylene group decreases the ρ -value by a factor of about 2.3 (varying from 1.7 to 2.9 in four examples).⁴⁴ These results tend to confirm the contention expressed in an earlier paper¹² that the observed ρ -values for the addition of the trichloromethyl radical to substituted 3-phenyl-1-propenes and 4-phenyl-1-butenes of -0.29 and -0.20 , respectively, are unexpectedly close together considering the presence of an additional insulating methylene group in the latter series. The two ρ -values differ by a factor of only 1.45.

Although the results discussed in this paper are in no way startling, it is nonetheless gratifying to see the regularity of the effects on reactivity of a vinyl group toward the trichloromethyl radical brought about by systematic structural changes in the rest of the molecule.

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TABLE II
RELATIVE RATES OF ADDITION OF $\text{Cl}_3\text{C}\cdot$ TO $\text{XCH}_2\text{CH}=\text{CH}_2$ AT 69.5°

X	σ^*	Rel. k
CN	+3.64 ^a	0.51 ± 0.04 ^c
Br	+2.80 ^a	0.64 ± 0.05
OH	+1.55 ^a	1.00
OCH ₃	+1.46 ^a	0.99 ± 0.02
CH ₂ CN	+1.30 ^b	1.03 ± .03
CH ₂ Br	+1.00 ^b	1.15 ± .10
CH ₂ OH	+0.555 ^b	1.51 ± .05

^a Ref. 32, p. 615. ^b Ref. 32, p. 619. ^c Average deviation.

TABLE III
RELATIVE RATES OF ADDITION OF $\text{Cl}_3\text{C}\cdot$ TO $\text{XCH}_2\text{CH}_2\text{CH}=\text{CH}_2$ AT 69.5°

X	σ^*	Rel. k
CN	+3.64 ^a	0.69 ± 0.02 ^c
Br	+2.80 ^a	0.76 ± 0.07
OH	+1.55 ^a	1.00
CH ₂ CN	+1.30 ^a	0.95 ± 0.10
CH ₂ Br	+1.00 ^b	1.03 ± .07
CH ₂ OH	+0.555 ^b	1.16 ± .03
<i>n</i> -C ₄ H ₉	-0.130 ^b	1.10 ± .07

^a Ref. 32, p. 615. ^b Ref. 32, p. 619. ^c Average deviation.

TABLE IV
RELATIVE RATES OF ADDITION OF $\text{Cl}_3\text{C}\cdot$ TO $\text{XCH}_2\text{CH}_2\text{CH}_2\text{CH}=\text{CH}_2$ AT 69.5°

X	σ^*	Rel. k
CN	+1.30 ^a	0.92 ± 0.01 ^c
Br	+1.00 ^a	0.87 ± 0.02
OH	+1.55 ^a	1.00
<i>n</i> -C ₃ H ₇	-0.115 ^b	1.09 ± 0.04

^a Ref. 32, p. 615. ^b Ref. 32, p. 619. ^c Average deviation.

TABLE V
 ρ^* -VALUES FOR THE REACTIONS
 $\text{X}(\text{CH}_2)_n\text{CH}=\text{CH}_2 + \text{Cl}_3\text{C}\cdot \rightarrow \text{X}(\text{CH}_2)_n\dot{\text{C}}\text{HCH}_2\text{CCl}_3$ AT 69.5°

<i>n</i>	ρ^*	r^a
1	-0.15 ± 0.01	-0.99
2	-.06 ± .01	-.95
3	-.024 ± .005	-.91

^a Correlation coefficient.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CALIFORNIA, SAN DIEGO, LA JOLLA, CALIF.]

Oxymercuration of Olefins. II. *cis*- and *trans*-Oxymercuration of Bicyclo[2.2.2]oct-2-ene

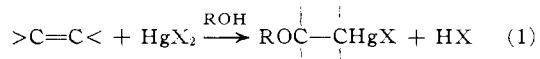
By T. G. TRAYLOR

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The oxymercuration of bicyclo[2.2.2]octene produces both *cis*- and *trans*-3-chloromercuribicyclo[2.2.2]octan-2-ol and no rearranged product, whereas under similar oxymercuration conditions norbornene gives only *cis* and cyclohexene only *trans* product. Hydroxymercuration of bicyclooctene in aqueous acetone is accompanied by *cis*-acetoxymercuration when mercuric acetate is used in high concentration or when sodium acetate is present. In glacial acetic acid oxymercuration of this olefin affords exclusively *cis* product. These and other data are presented as evidence that *cis*-oxymercuration of strained olefins occurs through an intermediate mercurinium ion. The results are consistent with a single intermediate leading to both *cis* and *trans* addition to bicyclooctene. This reaction also presents a simple synthesis of diastereomeric mercurials which are usually obtained with great difficulty.

Introduction

The oxymercuration of olefins, shown in eq. 1, displays kinetic and stereochemical behavior, solvent and



salt effects on rate and products, and structural effects which are typical of general electrophilic additions to double bonds.¹

However, some notable differences between this and other electrophilic additions are apparent. For exam-

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