

Experimental Section

Unless otherwise noted, the following general conditions were used in all reactions. Infrared spectra were recorded using either a Perkin-Elmer 137 Infracord or 710 grating spectrometer. NMR spectra were obtained with a Varian T-60 or Perkin-Elmer R24B spectrometer with tetramethylsilane as an internal standard. Ultraviolet spectra were obtained on a Perkin-Elmer 202 spectrometer. Mass spectral analysis and exact mass determinations were obtained from the Analytical Laboratory, College of Chemistry, University of California, Berkeley, Calif. Unless otherwise noted, all reactions run in nonaqueous media were maintained under an atmosphere of purified nitrogen. Diethyl ether and tetrahydrofuran were purified by distillation from sodium benzophenone. Mallinckrodt reagent grade dichloromethane was used without further purification. The formation of isophorone is representative of the procedure followed.

1,5,5-Trimethylcyclohex-2-en-1-ol (1).⁵ To a stirred solution of 5,5-dimethylcyclohex-2-en-1-one¹⁹ (2.0 g, 16.1 mmol) in 20 ml of anhydrous ether at -78°C was added, dropwise, an ethereal solution of methylolithium (11 ml of a 1.56 M ethereal solution). The resulting solution was allowed to warm to room temperature, stirred for 2.0 h, and quenched by the dropwise addition of 10 ml of water. The phases were separated and the aqueous layer extracted with two 10-ml portions of ether. The combined organic layers were washed with two 20-ml portions of water and dried over anhydrous MgSO_4 . The solvent was removed at reduced pressure to afford 2.15 g (96%) of a clear, colorless oil, judged by VPC²⁰ to be 97% pure. The alcohol was not purified further but used directly in the next step.

Isophorone (2). To a magnetically stirred slurry of pyridinium chlorochromate (4.30 g, 20.0 mmol) in 30 ml of dichloromethane, there was added in one portion a solution of 1 (1.40 g, 10.0 mmol) in 10 ml of dichloromethane at room temperature. The resulting dark red-black mixture was allowed to stir for 2.0 h at room temperature, and was diluted with an equal volume of ether. The ethereal solution was decanted from the black resinous polymer, which in turn was washed with three 20-ml portions of ether. The combined ethereal phases were washed successively with two 100-ml portions of 5% aqueous NaOH, 100 ml of 5% aqueous HCl, and two 50-ml portions of saturated aqueous NaHCO_3 , and dried over anhydrous MgSO_4 . The solvent was removed at reduced pressure and the residue bulb to bulb distilled to afford 1.33 g (96%) of isophorone ($\geq 97\%$ pure), spectrally identical with an authentic sample.

Registry No.—29, 930-39-2; cyclopropyl methyl ketone, 765-43-5.

Supplementary Material Available. Detailed experimental and spectroscopic data (IR, NMR, UV, mass spectrum) for compounds 3, 7, 9, 13, 14, 15, and 20 (11 pages). Ordering information is given on any current masthead page.

References and Notes

- (1) This work was supported in part by Grant AM-00709, National Institute of Arthritic, Metabolic, and Digestive Diseases, U.S. Public Health Service.
- (2) K. B. Sharpless and R. F. Lauer, *J. Am. Chem. Soc.*, **94**, 7154 (1972).
- (3) D. A. Evans and G. C. Andrews, *Acc. Chem. Res.*, **6**, 147 (1974), and references cited therein.
- (4) M. Moriwaki, S. Sawada, and Y. Inouye, *Chem. Commun.*, 419 (1970); V. Rautenstrauch, *Helv. Chim. Acta*, **56**, 2492 (1973).
- (5) P. S. Wharton and D. H. Bohler, *J. Org. Chem.*, **26**, 3615 (1961).
- (6) G. Büchi and J. C. Vederas, *J. Am. Chem. Soc.*, **94**, 9128 (1972).
- (7) B. M. Trost and J. L. Stanton, *J. Am. Chem. Soc.*, **97**, 4018 (1975).
- (8) J. H. Babler, D. O. Olsen, and W. H. Arnold, *J. Org. Chem.*, **39**, 1656 (1974); J. H. Babler and D. O. Olsen, *Tetrahedron Lett.*, 351 (1974); E. A. Braude, *Q. Rev., Chem. Soc.*, **4**, 404 (1950).
- (9) (a) E. Glotter, S. Greenfield, and D. Lavie, *J. Chem. Soc. C*, 1646 (1968); (b) E. Glotter, Y. Rabinsohn, and Y. Ozari, *J. Chem. Soc., Perkin Trans. 1*, 2104 (1975); (c) V. A. Petrow, *J. Chem. Soc.*, 998 (1939); (d) G. Büchi and D. Egger, *J. Org. Chem.*, **36**, 2021 (1971); (e) P. M. McCurry and R. K. Singh, *ibid.*, **39**, 2317 (1974); (f) P. Grieco, *ibid.*, **37**, 2363 (1972); (g) Y. Oshima, H. Yamamoto, and H. Nozaki, *J. Am. Chem. Soc.*, **95**, 4446 (1973); (h) J. S. Dutcher, J. G. MacMillan, and C. H. Heathcock, *J. Org. Chem.*, **41**, 2663 (1976).
- (10) For example see ref 11, 17, and E. J. Corey and C. W. J. Fleet, *Tetrahedron Lett.*, 4499 (1973); K. B. Sharpless and K. Akashi, *J. Am. Chem. Soc.*, **97**, 5927 (1975).
- (11) (a) E. J. Corey and J. W. Suggs, *Tetrahedron Lett.*, 2647 (1975). (b) After this manuscript was accepted for publication, J. H. Babler and M. J. Coghlin [*Synth. Commun.*, **6**, 469 (1976)] reported similar findings for some vinyl carbinols; their results can be compared with those reported in Table II.
- (12) The procedure reported in ref 9d was followed. Use of acetone as the solvent affords a slightly higher yield, as a mixture of α,β - and β,γ -enones in a 3:7 ratio, respectively. M. Haenel, unpublished results.
- (13) A. Marcou and H. Normant, *Bull. Soc. Chim. Fr.*, 3491 (1965).
- (14) For alternative methods see E. J. Corey, D. Enders, and M. G. Bock, *Tetrahedron Lett.*, 7 (1976), and ref 1-8 cited therein.
- (15) E. J. Corey, H. E. Ensley, and J. W. Suggs, *J. Org. Chem.*, **41**, 380 (1976).
- (16) Furthermore, it has been reported⁸ that attempted acid-catalyzed rearrangement of linalool afforded α -terpineol acetate as the major product, undetected in the present study.
- (17) J. C. Collins, W. W. Hess, and R. J. Frank, *Tetrahedron Lett.*, 3363 (1968); R. Ratcliffe and R. Rodehorst, *J. Org. Chem.*, **35** 4000 (1970).
- (18) Available from the Aldrich Chemical Co.
- (19) W. F. Gannon and H. O. House, "Organic Syntheses", Collect. Vol. V, Wiley, New York, N.Y., 1973, p 294.
- (20) VPC analysis was conducted using a 6 ft \times 0.25 in. 10% SE-30 on Chromosorb G (60/80 mesh) column.

Structure Effects in the Oxidation of Alkenes by Solutions of Thallic Salts¹

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The determination of polar, steric, and resonance effects in the oxidation of alkenes by solutions of thallic salts was carried out using the linear free energy relationship for the chosen set of $\text{RCH}=\text{CH}_2$, $\text{R}_1\text{R}_2\text{C}=\text{CH}_2$, and the internal alkenes; it was found that polar effects were the most important for the oxidation of $\text{RCH}=\text{CH}_2$ and $\text{R}_1\text{R}_2\text{C}=\text{CH}_2$ alkenes in this case. Both steric and resonance effects are important in the oxidation of internal alkenes. An aqueous medium is advantageous for the preparation of the carbonyl compounds from alkenes with electron-releasing substituents. The structure effects on the selectivity of the oxidation are discussed.

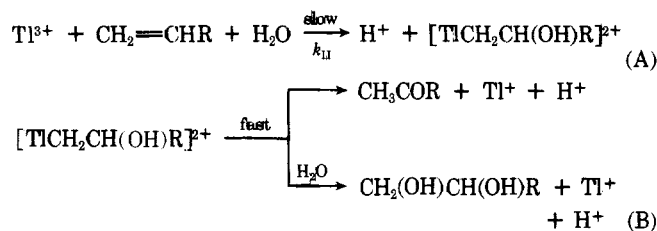
The oxidation of alkenes by thallic salts has been intensively studied from the point of view of the preparative organic chemistry,²⁻⁷ as well as from theoretical aspects.⁸⁻¹⁶ A more complete quantitative comparison of the influence of the individual parameters on the course of oxidation has been lacking so far.

The present investigation has been carried out to provide further information on the mechanism and the effect of

structure on the rates of oxidation of alkenes by thallic salts, and on the distribution of products of the oxidation.

The kinetic behavior of the lower alkenes (C_2 to C_4) during their reaction with thallic salts along with the distribution of the oxidation products are described in the fundamental studies of Henry.⁸ In aqueous medium, two characteristic products are formed by the oxidation of alkenes, viz. a carbonyl compound (an aldehyde or ketone) and vicinal diol. The

formation of these products, as well as their kinetics, has been explained by a generally adopted mechanism, whose principal features are shown in eq A and B:



The oxidation rates for alkenes are in accordance with the kinetic equation of the second order:

$$-d[\text{alkene}]/dt = -d[\text{TI}^{3+}]/dt = k_{\text{II}}[\text{TI}^{3+}][\text{alkene}] \quad (1)$$

The step determining the reaction rate is the formation of the intermediate hydroxythallation adduct according to eq A. The assumption that the formation of the intermediate adduct occurs as one step of the reaction is substantiated by the fact that the adduct could be isolated under favorable conditions.^{2,3,17} In addition, a spectral proof of the formation of the hydroxythallation adduct during the oxidation of alkenes in aqueous medium has also been presented.¹²

Experimental Section

Materials. The oxidation solution of thallium(III) sulfate was prepared as described previously.¹⁸ The concentration of thallium(III) was determined by two independent methods which yielded consistent results, namely (a) titration of iodine released by the reaction of TI^{3+} with KI with a standard solution of $\text{Na}_2\text{S}_2\text{O}_3$,¹⁹ and (b) by uv spectrophotometry.²⁰

2-Methyl-1-butene, 1-hexene, 1-heptene, 1-octene, 4-methyl-1-pentene, 3-methyl-1-butene, 1-nonene, 1-decene, 2-methyl-1-pentene, and 2-ethyl-1-hexene (all of a chromatographic purity minimum 99.8%) were prepared by pyrolysis of the acetate prepared by the acetylation of a corresponding alcohol according to a modified method.²¹ 2-Methyl-2-pentene, *trans*-4-methyl-2-pentene, and *cis*-4-methyl-2-pentene were obtained by isomerization of 4-methyl-1-pentene in the presence of PdCl_2 as a catalyst²² and with the subsequent rectification of the mixture of isomeric methylpentenes. 2,4,4-Trimethyl-2-pentene and 2,4,4-trimethyl-1-pentene were prepared according to our previous work.¹⁸ 1-Undecene, 1-dodecene, 1-tridecene, 1-tetradecene, 1-pentadecene, and 1-hexadecene (all of a chromatographic purity minimum 99.6%) were obtained by the redistillation of alkenes, supplied by the Research Institute of Crude Oil and Hydrocarbon Gases, Bratislava, and α -methylstyrene by the redistillation of the crude product supplied by Slovnaft, Bratislava (chromatographic purity minimum 99.9%).

The other chemicals used were commercial products of a reagent grade purity (Lachema, Brno).

Standards for GC-MS. Vicinal diols were prepared by the oxidation of corresponding alkenes with catalytic amounts of OsO_4 in anhydrous *tert*-butyl alcohol.²³

2-Pentanone, 3-hexanone, 2-hexanone, 2-methylbutanal, 2-ethylhexanal, and 2-octanone were prepared by the oxidation of the appropriate alcohols with $\text{Na}_2\text{Cr}_2\text{O}_7$.²³

2-Methyl-3-pentanone was prepared by pyrolysis of the mixture of barium isobutyrate and barium propionate and with the subsequent rectification of the crude product.

Analysis of the Oxidation Products. For the identification of the oxidation products and determination of their distribution, alkenes were oxidized using a relatively high initial concentration of thallium(III) sulfate. The standard reaction conditions were as follows: 150 ml of $\text{TI}_2(\text{SO}_4)_3$ ($[\text{TI}^{3+}]$ 0.370 mol/l.), 10 ml of alkene, $[\text{H}_2\text{SO}_4] = 1.254$ mol/l., $T = 20^\circ\text{C}$. The procedure was described in the our previous work.¹⁸

The glycols obtained were determined by the periodate method.²⁴ The GC-MS analysis was used for the determination of the other organic products.

GC. The products of oxidation were analyzed by a Fractovap 2300 (Carlo Erba, Milan) with a flame ionization detector. The column, length 2.5 m and diameter 2 mm, contained 10% polyethylene glycol adipate on Chromatone NAW DMCS. The working conditions follow:

temperature of the injector 175°C , temperature of the column 120°C ; the flow rates of N_2 , H_2 , and air were 35, 85, and 75 ml/min.

MS. The device was a MAT 111 GNOM (Varian). The chromatograph was equipped with a packing column (length 1 m, diameter 3 mm), isothermal at 105°C , flow rate of He 13 ml/min, energy of electrons 80 eV, intensity 270 mA, temperature of the ion source 200°C . The identity was found by comparison of the measured spectra with the authentic ones.

Kinetic Measurements. The kinetics of oxidation of alkenes by the aqueous solution of thallium(III) sulfate was followed by uv spectrophotometrically in the wavelength range of 200–240 nm by measuring the decrease of absorbance caused by the decrease of concentration of the TI^{3+} ions. The kinetic measurements were carried out using concentrations appropriate to the spectral technique, i.e., with the concentration of TI^{3+} ions 2.5×10^{-5} to 2.0×10^{-4} mol/l. and that of the alkene 2.5×10^{-4} to 2.0×10^{-3} mol/l. The concentration of sulfuric acid was 0.05 mol/l. ($\mu = 0.15$ M) in all cases. The rates of reaction with half-lives less than 30 s were determined by applying the stopped-flow method on a spectrophotometer (Durrum-Gibson D-110), while the rates of slower reactions were measured in a spectrophotometer (VSU-2-P, Zeiss, Jena). The reaction temperature of 25°C was kept at a chosen level within the limit of $\pm 0.1^\circ\text{C}$.

Results and Discussion

The results have been analyzed to provide a quantitative evaluation of the contributions of polar, steric, and resonance effects to the free energy of activation.

By using the principle of additivity we can consider in the first approximation the steric (S) and polar (P) effects to be different functions of structure, originating from independent quantities. (However, the resonance effects are not independent of the steric effects.²⁵) Then, the full "polar-steric" Taft equation may be written using a common standard (in the case of alkenes CH_3):

$$\log(k/k_0) = \rho^* \Sigma \sigma^* + \delta \Sigma E_s \quad (2)$$

Some reactions may be correlated with the solely polar portion of the equation. The validity of these considerations was ascertained on the model whose reaction center is represented by the C=C bond.

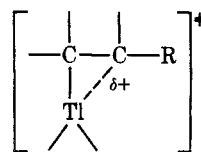
The kinetics of the hydroxythallation were followed in accordance with our earlier work.²⁶ These reactions exhibited second-order kinetics corresponding to the rate law defined by eq 1. The alkene was always in sufficient excess over TI^{3+} so that the observed kinetics were pseudo-first-order (eq 3).

$$-d \ln [\text{TI}^{3+}]/dt = k_{\text{obsd}} = k_{\text{II}}[\text{alkene}] \quad (3)$$

The values of k_{II} are listed in Table I.

The linear free energy-polar energy relationship is depicted in Figure 1 in the form of a plot of $\log k_{\text{II}}$ (for $\text{RCH}=\text{CH}_2$) vs. Taft σ^* for R.²⁷ There is fulfilled the condition of constant mechanism, i.e., the transition state geometry is (approximately) unchanged; only the distribution of charge during the reaction is changed.²⁸

The slope for the dependence of $\log k_{\text{II}}$ vs. σ^* has a value of $\rho^* = -3.00 \pm 0.05$, which indicates that in the transition state of the reaction, the positive charge is highly localized at the carbon atom (approaching thus in its nature the carbonium ion), to which the substituent R is attached:



A similar correlation has been found for the oxidation of alkenols by thallium(III) perchlorate in aqueous medium,¹² with $\rho^* = -3.2$. The concept concerning the nature of the transition state occurring during the oxidation of thallic ions is, in addition, supported by the character of analogous reaction be-

Table I. Values of the Rate Constants of the Second Order for Oxidation of Alkenes by Thallium(III) Sulfate in Aqueous Sulfuric Acid at 25 °C

Registry no.	No.	Alkene	k_{II} , l. mol ⁻¹ s ⁻¹
	1	Ethylene ^a	0.335 ± 0.002
	2	Propylene ^a	9.423 ± 0.067
	3	1-Butene ^a	18.80 ± 0.132
109-67-1	4	1-Pentene	20.85 ± 0.146
592-41-6	5	1-Hexene	25.72 ± 0.180
592-76-7	6	1-Heptene	14.91 ± 0.104
111-66-0	7	1-Octene	8.40 ± 0.059
107-18-6	8	Allyl alcohol	0.25 ± 0.002
691-37-2	9	4-Methyl-1-pentene	19.80 ± 0.139
563-45-1	10	3-Methyl-1-butene	35.01 ± 0.245
124-11-8	11	1-Nonene	2.30 ± 0.016
872-05-9	12	1-Decene	2.51 ± 0.018
821-95-4	13	1-Undecene	3.42 ± 0.024
112-41-4	14	1-Dodecene	1.50 ± 0.011
2437-56-1	15	1-Tridecene	0.214 ± 0.002
1120-36-1	16	1-Tetradecene	0.390 ± 0.003
13360-61-7	17	1-Pentadecene	0.491 ± 0.003
629-73-2	18	1-Hexadecene	0.230 ± 0.002
627-40-7	19	Methyl allyl ether	0.260 ± 0.002
927-73-1	20	4-Chloro-1-butene	0.660 ± 0.005
100-42-5	21	Styrene	1.160 ± 0.008
625-27-4	22	2-Methyl-2-pentene	49.60 ± 0.35
674-76-0	23	<i>trans</i> -4-Methyl-2-pentene	81.90 ± 0.57
691-38-3	24	<i>cis</i> -4-Methyl-2-pentene	23.80 ± 0.17
107-40-4	25	2,4,4-Trimethyl-2-pentene	2.14 ± 0.01
763-29-1	26	2-Methyl-1-pentene	27.80 ± 0.19
107-39-1	27	2,4,4-Trimethyl-1-pentene	13.00 ± 0.09
1632-16-2	28	2-Ethyl-1-hexene	22.03 ± 0.56
98-83-9	29	α -Methylstyrene	1.79 ± 0.01

^a Values were calculated from the data in ref 8.

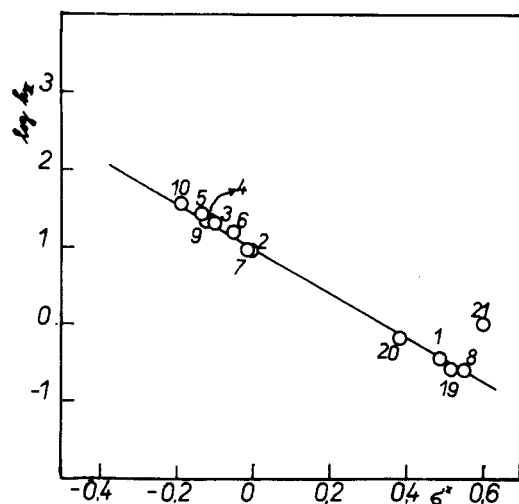


Figure 1. Verification of the Taft equation for the oxidation of $RCH=CH_2$ alkenes by thallium(III) sulfate at 25 °C: $R = 0.999$, $S = 99.80\%$, $\alpha = 2.41$.

tween mercuric ions (Hg^{2+} is isoelectronic with Tl^{3+}) and alkenes in water, resulting in stable hydroxymercuration adducts. For this reaction, Halpern and Tinker²⁹ found a correlation between reactivity of alkene and its structure ($\rho^* = -3.3$), which again is in accordance with the idea of the transition state with a character approaching that of the carbonium ion. A completely free (open) carbonium ion, however, can be ruled out for the hydroxymercuration, as the *cis*-*trans* isomerization of internal olefins, such as that of *cis*- or *trans*-butene³⁰ or *cis*-stilbene,³¹ has not been observed during that reaction.³²

In order to evaluate quantitatively the structure effects in

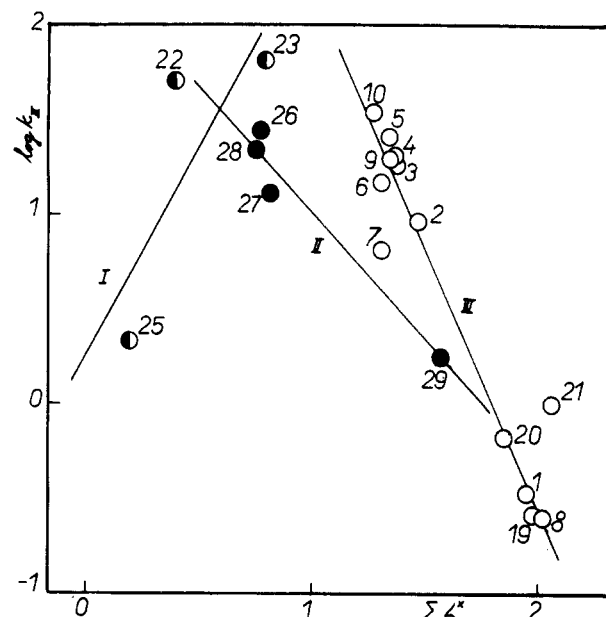


Figure 2. LFE-PE relationship of the oxidation of $R_1R_2C=CR_3R_4$ alkenes by thallium(III) sulfate at 25 °C: I, oxidation of internal alkenes, ●; II, oxidation of $R_1R_2C=CH_2$ alkenes, ●; III, oxidation of $RCH=CH_2$ alkenes, ○.

the case of internal alkenes, it was necessary to introduce the hypothesis of the additivity polar and steric effects (Table II).

The measure of the validity of the additivity principle of polar effects is illustrated in Figure 2.

Palm³³ showed that for the quantitative evaluation of steric effects it is necessary to introduce other variables, resonance

Table II. Principle of Additivity for $R_1R_2C=CR_3R_4$ Alkenes

No.	Substituent				$\Sigma\sigma^*{}^a$	ΣE_s^b
	R_1	R_2	R_3	R_4		
1	H	H	H	H	1.960	4.96
2	CH ₃	H	H	H	1.470	3.72
3	C ₂ H ₅	H	H	H	1.370	3.65
4	<i>n</i> -C ₃ H ₇	H	H	H	1.355	3.36
5	<i>n</i> -C ₄ H ₉	H	H	H	1.340	3.33
6	<i>n</i> -C ₅ H ₁₁	H	H	H	1.310	3.32
7	<i>n</i> -C ₆ H ₁₃	H	H	H	1.310	3.31
8	CH ₂ OH	H	H	H	2.025	5.18
9	<i>i</i> -C ₄ H ₉	H	H	H	1.345	2.79
10	<i>i</i> -C ₃ H ₇	H	H	H	1.280	3.25
19	CH ₃ OCH ₂	H	H	H	1.990	3.53
20	Cl(CH ₂) ₂	H	H	H	1.855	2.82
21	C ₆ H ₅	H	H	H	2.070	4.96 ^b
22	CH ₃	CH ₃	H	C ₂ H ₅	0.390	1.17
23	CH ₃	H	H	<i>i</i> -C ₃ H ₇	0.790	2.01
25	CH ₃	CH ₃	H	<i>t</i> -C ₄ H ₉	0.190	-0.30
26	<i>n</i> -C ₃ H ₇	CH ₃	H	H	0.765	2.12
27	neo-C ₅ H ₁₁	CH ₃	H	H	0.815	0.74
28	<i>n</i> -C ₄ H ₉	C ₂ H ₅	H	H	0.750	2.02
29	C ₆ H ₅	CH ₃	H	H	1.580	-0.07 ^c

^a Values were calculated from the data in ref 27. ^b Values were calculated from the data in ref 25. ^c Value was calculated from the data in ref 34.

Table III. Regression Analysis

Eq	$\log k_{11} = \rho^*\Sigma\sigma^* + b$				$\log k_{11} = \delta\Sigma E_s + c$				$\log k_{11} = \delta\Sigma E_s^0 + d$			
	ρ^*	b	$S, \%$	R	δ	c	$S, \%$	R	δ	d	$S, \%$	R
RCH=CH ₂	-2.91 ± 0.08	6.35	95.45	0.977	-0.92 ± 0.06	6.66	84.46	0.919	-0.78 ± 0.10	5.62	77.26	0.879
Internal alkenes ^d			64.32	0.802			94.67	0.973			98.01	0.990
$R_1R_2C=CH_2^a$			95.45	0.977			86.12	0.928			81.72	0.904

^a There are not enough compounds to attempt a correlation slope.

effects and the nonclassical bonding interactions, which can be included as a contribution of the C-C as well as the C-H hyperconjugation to E_s . In this way, one gets the new "right steric constant" E_s^0 :

$$E_s^0 = E_s + 0.33(n_H - 3) + 0.13n_C \quad (4)$$

Results of these relationships are in Table III. From Table III it is obvious that oxidation of RCH=CH₂ alkenes by thallium(III) sulfate in aqueous medium may be correlated with solely the polar Taft equation. In addition, from here it can be seen that steric and resonance effects are the most important factors in the oxidation of internal alkenes. The relatively considerable importance of the resonance effects in this case explains the observed isomerization of the oxidation of 2,4,4-trimethyl-2-pentene.¹⁸

The combined linear free energy-polar energy and steric energy relationship is best expressed, for the oxidation of $R_1R_2C=CR_3R_4$ alkenes, by the modified eq 2. Using a multiple linear regression analysis it is found that the rates of oxidation are satisfactorily fitted by eq 5:

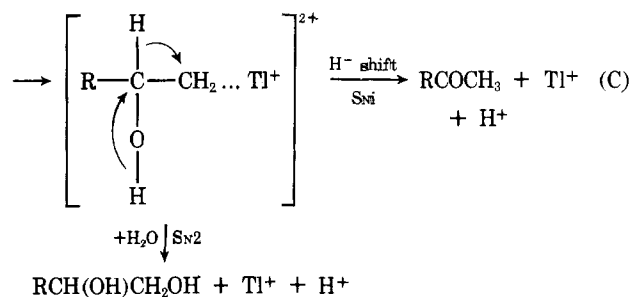
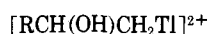
$$\log k_{11} = -(2.75 \pm 0.37)\Sigma\sigma^* + (0.97 \pm 0.41)\Sigma E_s + (3.24 \pm 0.94) \quad (5)$$

The correlation coefficient is 0.946; the scope of validity 89.49%. Representation of this relationship is in Figure 3.

A similar conclusion has been found for the bromination of mono-, di-, tri-, and tetrasubstituted olefins.³⁶

The second stage of reaction which, according to the interpretation that we have adopted, corresponds to the dethallation step and formation of the final oxidation products (eq B), was examined from point of view of selectivity. For these

substrates the proposed dethallation step, following the interpretations of Henry⁸ and other previous workers, can be represented as



There is the case when a compound satisfying the structural assumption for a given empirical relationship undergoes two concurrent reactions of the same order (to the intermediate hydroxythallation adduct). Then, according to absolute rate theory,³⁵ the ratio of the amounts of both products X_c/X_g is independent of time and equal to the ratio of the two kinetic constants k_c/k_g .

$$\log(X_c/X_g) = \log(k_c/k_g) = (\rho_c^* - \rho_g^*)\sigma^* + \log(k_c^0/k_g^0) \quad (6)$$

For the oxidation of RCH=CH₂ and $R_1R_2C=CH_2$ the dependence of the yield of the carbonyl (X_c) and glycol (X_g) on the substituent R was investigated (Table IV, Figure 4).

A quantitative estimation (Table III) suggested that the effect of the substitution is exclusively polar. The slope in

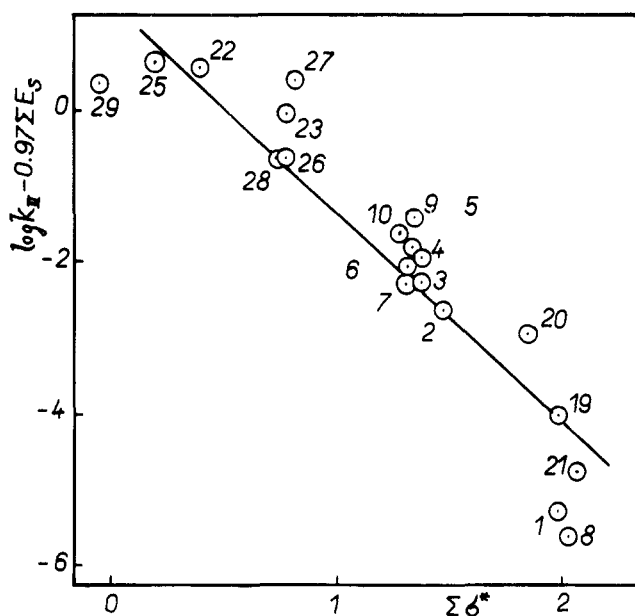


Figure 3. Reactivity of $R_1R_2C=CR_3R_4$ alkenes in the oxidation by thallium(III) sulfate in aqueous medium as a function of polar and steric effects at 25 °C.

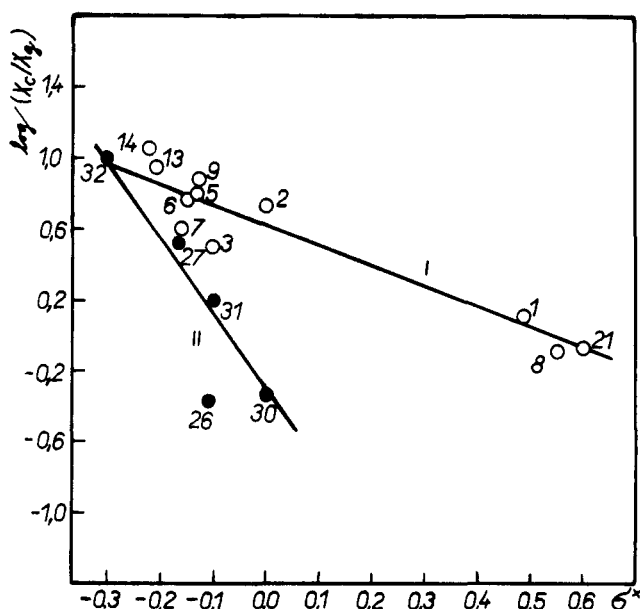


Figure 4. Dependence of selectivity on the structure of alkenes for their oxidation by thallium(III) sulfate at 20 °C.³⁷ I, oxidation of $RCH=CH_2$ alkenes, $(\rho_c^* - \rho_g^*) = -1.20 \pm 0.15$, $\log(k_c^0/k_g^0) = 1.05$, $R = 0.950$, $S = 90.25\%$; II, oxidation of $R_1R_2C=CH_2$ alkenes, $(\rho_c^* - \rho_g^*) = -4.39 \pm 0.09$, $\log(k_c^0/k_g^0) = 3.52$, $R = 0.996$, $S = 99.20\%$.

Figure 4 (I), equal to -1.20 ± 0.15 , has relatively a lower value, and is in agreement with the assumption of the S_N2 mechanism of the formation of vicinal glycol (eq C). The individual values of ρ_c^* and ρ_g^* cannot be determined, however, although it can be assumed with certainty that $|\rho_c^*| > |\rho_g^*|$ and hence $\rho_c^* < 0$. The assumption according to which ρ_g^* would be positive is quite acceptable. The effect on the migration aptitude of H^- , giving carbonyl product, is increased with electron-releasing substituents.

In the case of $R_1R_2C=CH_2$ alkenes it was considered necessary to stick to series with one constant substituent (CH_3). The correlation for these alkenes (Figure 4, II) has a considerable negative slope (-4.39 ± 0.09). The high absolute value of ρ^* is in agreement with the substitution directly in the $C=C$

Table IV. Structure Effects on the Distribution of Products of the Oxidation of $RCH=CH_2$ and $R_1R_2C=CH_2$ Alkenes by Thallium(III) Sulfate at 20 °C

$RCH=CH_2$	Mol fraction		$\Delta\Delta G^\ddagger = -2.303RT \log(X_c/X_g)$, kcal ^b
	Carbonyl ^f	Glycol	
H ^a	0.565	0.435	-0.15 ± 0.01
CH ₃ ^a	0.840	0.160	-0.98 ± 0.03
C ₂ H ₅ ^a	0.760	0.240	-0.67 ± 0.02
<i>n</i> -C ₄ H ₉	0.865	0.135	-1.07 ± 0.06
<i>i</i> -C ₄ H ₉	0.882	0.118	-1.17 ± 0.07
<i>n</i> -C ₅ H ₁₁	0.853	0.147	-1.03 ± 0.04
<i>n</i> -C ₆ H ₁₃	0.795	0.205	-0.79 ± 0.02
<i>n</i> -C ₉ H ₁₉	0.901	0.099	-1.28 ± 0.04
<i>n</i> -C ₁₀ H ₂₁	0.920	0.080	-1.42 ± 0.06
C ₆ H ₅	0.461 ^c	0.539	0.09 ± 0.01
CH ₂ OH	0.448 ^d	0.552	0.12 ± 0.01
$R(CH_3)C=CH_2$			
CH ₃ ^{a,g}	0.455	0.545	0.46 ± 0.02
C ₂ H ₅ ^h	0.607	0.393	-0.25 ± 0.01
<i>n</i> -C ₃ H ₇	0.274	0.610	0.47 ± 0.02
<i>t</i> -C ₄ H ₉ ⁱ	0.905	0.095	-1.31 ± 0.07
neo-C ₅ H ₁₁ ^e	0.244	0.073	-0.70 ± 0.04

^a Values from ref 8. ^b $\Delta\Delta G^\ddagger = \Delta G_c^\ddagger - \Delta G_g^\ddagger$. ^c Phenylacetaldehyde. ^d Hydroxyacetone. ^e Others are the aldolization products. ^f Ketone ($RCH=CH_2$), ketones and aldehyde together ($R_1R_2C=CH_2$). ^g Registry no., 115-11-7. ^h Registry no., 563-46-2. ⁱ Registry no., 594-56-9.

bond. There is the possibility that the R_1 and R_2 groups rearrange simultaneously with splitting off of the $C-Tl$ bond and are completely rearranged by the time the Tl is detached.

Registry No.—Thallium(III) sulfate, 16222-66-5.

References and Notes

- (1) Part 1 in the series Extrathermodynamic Free Energy Relationships in the Oxidation of Alkenes by Thallic Salts.
- (2) H. J. Kabbe, *Justus Liebigs Ann. Chem.*, **656**, 204 (1962).
- (3) W. Kruse and T. M. Bednarski, *J. Org. Chem.*, **36**, 1154 (1971).
- (4) F. Goodridge and C. J. H. King, *J. Appl. Chem. Biotechnol.*, **21**, 208 (1971).
- (5) D. Farcasiu, R. Schleyer, and D. B. Ledlie, *J. Org. Chem.*, **38**, 3455 (1973).
- (6) A. McKillop, J. D. Hunt, F. Kienzle, E. Bigham, and E. C. Taylor, *J. Am. Chem. Soc.*, **95**, 3635 (1973).
- (7) P. K. Grant, T. L. Liau, and Kun-She Low, *Aust. J. Chem.*, **28**, 903 (1975).
- (8) P. M. Henry, *J. Am. Chem. Soc.*, **87**, 990, 4423 (1965); **88**, 1597 (1966); *Adv. Chem. Ser.*, **70**, 126 (1968).
- (9) R. J. Ouellette, G. Kordosky, C. Lewin, and S. Williams, *J. Org. Chem.*, **34**, 4104 (1969).
- (10) L. Nadon, M. Tardat, M. Zador, and S. Fliszar, *Can. J. Chem.*, **51**, 2366 (1973).
- (11) C. Freppel, R. Favier, J.-C. Richter, and M. Zador, *Can. J. Chem.*, **49**, 2586 (1971).
- (12) J. E. Byrd and J. Halpern, *J. Am. Chem. Soc.*, **95**, 2586 (1973).
- (13) P. Abley, J. E. Byrd, and J. Halpern, *J. Am. Chem. Soc.*, **95**, 2591 (1973).
- (14) L. Nadon and M. Zador, *Can. J. Chem.*, **52**, 2667 (1974).
- (15) J. Grignon and S. Fliszar, *Can. J. Chem.*, **52**, 3209 (1974).
- (16) J. Urbanec, M. Strasak, J. Vojtko, and M. Hrusovsky, *Collect. Czech. Chem. Commun.*, **41**, 611 (1976).
- (17) S. Uemura, K. Zushi, A. Tabata, A. Toshimitsu, and H. Okano, *Bull. Chem. Soc. Jpn.*, **47**, 920 (1974).
- (18) M. Strasak, M. Hrusovsky, J. Urbanec, J. Vojtko, and S. Gregus, *Chem. Zvesti*, in press.
- (19) I. M. Korenman, "Analiticheskaya Khimiya Talliya", Izdatel'stvo Akademii Nauk SSSR, Moscow, 1960.
- (20) T. E. Rogers and G. M. Waind, *Trans. Faraday Soc.*, **57**, 1360 (1961).
- (21) W. J. Bailey, *J. Org. Chem.*, **21**, 543 (1956).
- (22) H. B. Sparke, M. Turner, and J. M. Wenham, *J. Catal.*, **4**, 332 (1965).
- (23) M. Marko and L. Krasnec, "Fundamentals of Preparative Organic Chemistry", SVTL Bratislava, 1962.
- (24) G. O. Curme, "Glycols", Reinhold, New York, N.Y., 1952, p 337.
- (25) P. R. Weiss, *Chem. Rev.*, **63**, 171 (1963).
- (26) J. Urbanec, M. Strasak, M. Hrusovsky, and J. Vojtko, *Collect. Czech. Chem. Commun.*, **41**, 604 (1976).
- (27) The values of σ^* from R. W. Taft in "Steric Effects in Organic Chemistry", M. S. Newman, Ed., Wiley, New York, N.Y., 1956, Chapter 13.
- (28) O. Exner in "Advances in Linear Free Energy Relationships", N. B. Chapman and J. Shorter, Ed., Plenum Press, New York, N.Y., 1972, Chapter 1.

- (29) J. Halpern and H. B. Tinker, *J. Am. Chem. Soc.*, **89**, 6427 (1967).
 (30) M. H. Kreevoy, L. L. Schaleger, and J. C. Ware, *Trans. Faraday Soc.*, **58**, 2433 (1962).
 (31) M. H. Kreevoy, N. Takashina, and L. L. Schaleger, Abstracts, 137th National Meeting of the American Chemical Society, Cleveland, Ohio, April 1960.
 (32) From Figure 1 it can be seen that point 21 (oxidation of styrene) is off the line. This can be explained by the fact that there is a resonance effect present. In the graph (Figure 1) values for the alkenes 11–18 are not plotted. The substituents on these alkenes are too great already so that they may cause rotation (mobile substituents) and hence hinder the admission of the thallic ion to the reaction center—this is against the principle of the conservation of rigidity.²⁸ In this way we have explained the relative low values of rate constants in comparison with the other $RCH=CH_2$ alkenes.
 (33) V. A. Palm, *Usp. Khim.*, **30**, 1069 (1961); "Osnovy Kolichestvennoi Teorii Organicheskikh Reaktsii", Khimiya, Leningrad, 1967, p. 173.
 (34) J. Shorter, *Q. Rev., Chem. Soc.*, **24**, 433 (1970).
 (35) J. E. Leffler and E. Grunwald, "Rates and Equilibria of Organic Reactions", Wiley, New York, N.Y., 1963, p. 162.
 (36) G. Mouvier and J. E. Dubois, *Bull. Soc. Chim. Fr.*, 1441 (1968).
 (37) Number of alkenes see Table I. The other ones are **30** (isobutene), **31** (2-methyl-1-butene), **32** (2,3,3-trimethyl-1-butene).
 (38) The following symbols are used: LFER, linear free energy relationships; PE, polar energy; SE, steric energy; σ^+ , electrostatic and electronic effect of substituent (with respect to CH_3); ρ^+ , parameter characteristic the sensibility of reaction to polar effects; E_s , steric parameter of substituent with respect to CH_3 (Taft); E_s^0 , "right steric parameter" (Palm); δ , parameter characteristic the sensibility of reaction to steric effects; n_H , number of C–H bonds in α position with respect to substituent; n_C , number of C–C bonds in α position with respect to substituent; R , regression coefficient; $S = 100R^2$, the number of experimental results (%) that can be brought objectively into context with the linear regression relation.

Cationic Polymerizations by Aromatic Initiating Systems.

1. A Model for Initiation and Termination Using the

p-CH₃C₆H₄CH₂Cl/Et₃Al System

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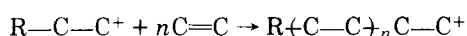
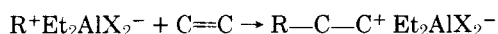
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The interaction between *p*-CH₃C₆H₄CH₂Cl and Et₃Al (or Et₂AlCl) has been investigated using CH₂Cl₂ solvent in the range from –50 to –80 °C. The reaction yields three products: *p*-CH₃C₆H₄CH₂Et, *p*-CH₃C₆H₄CH₂H, and oligomeric polybenzyls. The first two arise upon ethylation and hydridation of the *p*-CH₃C₆H₄⁺CH₂ cation by the Et₃AlCl[–] counteranion while the third one is the result of self-polybenzylation. The relative amounts of termination products and polybenzyls can be controlled by temperature and reagent stoichiometry (Al/Cl ratio). Surprisingly, fastest *p*-CH₃C₆H₄CH₂Cl disappearance was observed at low Al/Cl ratios. Kinetic studies indicate that ethylation and hydridation occur readily with Et₃Al, i.e., via the *p*-CH₃C₆H₄⁺CH₂ Et₃AlCl[–] pair, while the in situ formation of Et₂AlCl leads to the *p*-CH₃C₆H₄⁺CH₂ Et₂AlCl₂[–] pair which in turn gives rise mainly to polybenzyls. The understanding of the mechanism of ethylation and hydridation in the *p*-CH₃C₆H₄CH₂Cl/Et₃Al reaction is important as a model of initiation followed by immediate termination of cationic polymerizations by benzyl halide/alkylaluminum initiator systems.

During our fundamental studies on the mechanism of cationic olefin polymerizations it appeared of interest to investigate the mechanism of initiation by the use of aromatic cations, in particular to study the initiation of isobutylene polymerization by the CH₃C₆H₄⁺CH₂ cation and thus to introduce a UV-active *p*-methylbenzyl head group into a polyisobutylene chain. Quantitative analysis of UV-active aromatic head groups promised to provide increased insight into the mechanistic details of initiation and chain breaking.

We have shown that isobutylene polymerization can be initiated readily by the use of a variety of tertiary alkyl and allyl halides in conjunction with alkylaluminum compounds,^{1,2} presumably by direct alkylation of the olefin:



R = tertiary alkyl or allyl, X = halide

This paper concerns the interaction between the benzyl halide (initiator) and alkylaluminum (coinitiator) in the absence of olefin and the effect of experimental variables on the reaction. Subsequent papers of this series will deal with further model studies and polymerizations.

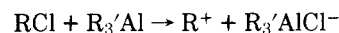
Because benzyl chloride in the presence of Friedel–Crafts acids readily undergoes self-benzylation and rapidly leads to polybenzyls,⁶ an undesirable side reaction for our study, we used the *p*-methyl substituted derivative, *p*-methylbenzyl

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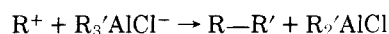
chloride, to afford at least some protection against para self-benzylation and to increase the reaction rate.

Results and Discussion

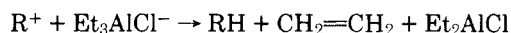
A. Interaction between *p*-Methylbenzyl Chloride and Triethylaluminum. The reaction between alkyl chlorides and alkylaluminums may be viewed as a model for initiation followed by immediate termination in carbenium ion polymerization ("polymerization without propagation").^{1,2} In particular, the first step is the generation of a carbenium ion R⁺



which in the absence of monomer is rapidly followed by the collapse of the cation–counterion pair by alkylation



or by hydridation if a β hydrogen with respect to aluminum is available:^{2–4}



With aromatic carbenium ion sources, specifically with *p*-methylbenzyl chloride and triethylaluminum, the following reactions are expected to occur:

