SINGLE-PARAMETER VERSUS DUAL-PARAMETER CORRELATION FOR RADICAL REACTIONS. ADDITION OF BROMINE ATOMS TO α-METHYLSTYRENES

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A rigorous procedure was developed for measuring the relative rates of addition of bromine atoms to eleven substituted α-methylstyrenes (1-Y, with Y = CF$_3$, NO$_2$, F, CN, Cl, Br, CO$_2$Me, Me, COMe, OMe and SMe). The reaction was run in tetrahydrofuran in the presence of HBr, O$_2$ and dibutyl peroxyoxalate at 30 °C. All products were derived from the YC$_6$H$_4$CMeCH$_2$Br adduct radicals, which were immediately intercepted by O$_2$. Correlation analysis of all the data confirmed the proposition that in the absence of measurable steric effects, the relative rates for radical additions can be correlated only by a dual-parameter equation and not by a single-parameter equation. Among various combinations of σ^* and σ^x, the ($\sigma_{JJ}^* + \sigma_{mb}$) combination yields the best correlation.

INTRODUCTION

Polar (including resonance polar) effects and spin-delocalization effects of substituents are independent of each other. This view or proposition is supported, for instance, by the fact that (1) both electron-pair acceptors and electron-pair donors can be effective spin-delocalizing substituents,[1] and (2) polar substituent-constant (σ^x) scales[2] are not correlatable with spin-delocalization (σ^*) scales (see below).[1,3] We would expect, then, that in the absence of measurable steric effects, rates of radical reactions should be correlated by the dual-parameter equation (1) rather than by the single-parameter equation (2):

$$\log k_Y/k_H = \rho^x\sigma^x + \rho^*\sigma^* \qquad (1)$$

$$\log k_Y/k_H = \rho^x\sigma^x \qquad (2)$$

if the particular transition-state (TS) structure involved is not perfectly symmetrical, or is not dominated by polar effects. One puzzling and intriguing problem in radical chemistry today is, therefore, why so many radical reactions have been claimed to be correlatable by the single-parameter equation (2),[4] even though dual-parameter correlations in various forms have been proposed by different authors over the years.[5]

Possible causes could be one or more of the following circumstances. (1) The kinetic method used might not be the most rigorous, e.g. insufficient measurements were performed over a wide range of the extent of reaction.[4,5] (2) The reaction studied was not clean enough (cf. Dust and Arnold's comment in Ref. 6 on Jackson's approach). (3) The number of well distributed substituents used was not large enough.[7] (4) The polar effects greatly predominate over the spin-delocalization effect for that particular TS being studied. One possible example could be the hydrogen-atom abstraction reaction in which a σ-bond is being broken. (5) Most of the previous 'successful' correlations by equation (2) used σ^+ (cf. Ref. 2) for σ^x. It is of special interest to note that there is a much higher degree of 'parallelism' between σ_{JJ}^* and σ^+ than those between σ_{JJ}^* and any other σ^x.

The σ_{JJ}^* scale is the most self-consistent and cross-checked scale of spin-delocalization substituent constants now available.[1,8] It is based on the ^{19}F NMR data of substituted α,α,β-trifluorostyrenes and the rate constants of their thermal cycloaddition reactions. The σ_{mb} scale of polar substituent constants is derived from the above-mentioned ^{19}F NMR data,[9] hence it is best suited for applications to systems with substituents interacting directly (via polar resonance and/or field effects) with a
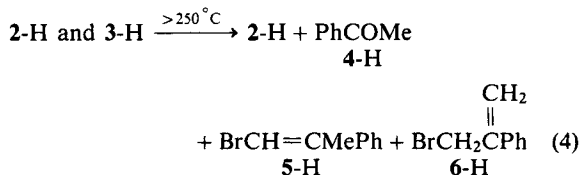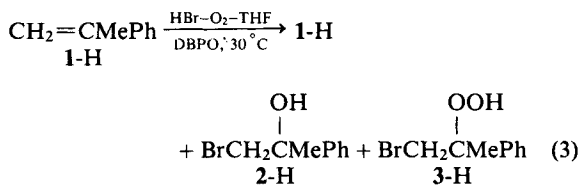
double bond. For instance, the σ_{mb} constants are direct measures of the degree of π-bond polarization of substituted styrenes (cf. Ref. 9 and references cited therein). The correlation coefficients between σ_{JJ}^* and various σ^x are as follows: σ^+, $0\cdot419$ ($n = 18$); σ^- (cf. Ref. 27), $0\cdot169$ ($n = 11$); σ_p, $0\cdot092$ ($n = 22$); σ_{mb},[8] $0\cdot075$ ($n = 22$); σ_R (polar substituent constant for the resonance effect, cf. Ref. 2d), $0\cdot118$ ($n = 22$); and σ_F (polar substituent constant for the field effect, cf. Ref. 2d), $0\cdot015$ ($n = 22$).

On the basis of the above mentioned considerations and with the objective of addressing the single-parameter versus dual-parameter problem together with other schools of workers, we suggested the following requirements or conditions for performing a reliable correlation analysis on radical reactions or properties:[7b,8] (i) at least 11–12 substituents with well distributed electronic effects should be used; (ii) the measured rate should be the rate of the rate-limiting elementary step; (iii) the reaction should be exceptionally clean and, if otherwise, i.e. if several products are formed, then all of them should be derived from the same measured step; and (iv) a rigorous kinetic procedure should be followed, for example, several (e.g. 5–8) measurements of the relative rates $[k_Y/k_H = k_r(Y)]$ are performed over a reasonably wide range of the degree of conversion (extent of reaction), which can be inversely expressed in terms of φ values, where φ is the mole fraction of unreacted substrates at a particular reaction time. The reliability of this kinetic methodology can be evaluated from the deviations of the independently measured (5–8) $k_r(Y)$ values from the averaged value (either the arithmetic average or that obtained from the regression line, see Experimental). Regrettably, we are not aware of previous work which fulfils all the above-mentioned conditions. This work was carried out concurrently with parallel work which fulfils these conditions.[8]

Consideration of point (5) above led us to pick an addition reaction to *para*-substituted styrenes for verifying the necessity to use the dual-parameter equation (1) for the simple reason that the substituents are already in full conjugation with the π-bonds before they are homolytically cleaved by attacking radicals. In other words, if correlation by equation (1) did not give a significant improvement over that by equation (2) for an addition reaction, we would also be tempted to believe that there were no need for a σ^* scale. Another equally important reason for selecting the aforesaid reaction is the fact that we now possess a tailor-made σ^x scale, i.e. σ_{mb} (see above), for evaluating the polar effect on this radical addition reaction to styrenes.[1,8,9] The problem of whether the σ_{mb} scale is better than the other σ^x scales (e.g. σ^+ or σ_p) for these addition reactions can be solved by comparing results of correlation analysis with $\sigma^* + \sigma_{mb}$, $\sigma^* + \sigma^+$, $\sigma^* + \sigma_p$, etc.

After much exploration, we finally succeeded in finding the desired addition reaction and in working out for this reaction a kinetic methodology that satisfied all our requirements proposed above. As shown in equations (3) and (4):

$$CH_2{=}CMePh \xrightarrow[\text{DBPO, } 30\,^\circ C]{\text{HBr–O}_2\text{–THF}} \text{1-H}$$
$$\text{1-H}$$

$$+ \underset{\text{2-H}}{BrCH_2\overset{\overset{\displaystyle OH}{|}}{C}MePh} + \underset{\text{3-H}}{BrCH_2\overset{\overset{\displaystyle OOH}{|}}{C}MePh} \quad (3)$$

$$\text{2-H and 3-H} \xrightarrow{>250\,^\circ C} \text{2-H} + \underset{\text{4-H}}{PhCOMe}$$

$$+ \underset{\text{5-H}}{BrCH{=}CMePh} + \underset{\text{6-H}}{BrCH_2\overset{\overset{\displaystyle CH_2}{\|}}{C}Ph} \quad (4)$$

the reaction is that of α-methylstyrene (1-H) with HBr and O_2 in tetrahydrofuran (THF) at $30\,^\circ C$ in the presence of the initiator di-*tert*-butyl peroxyoxalate (DBPO), The initial crude product is composed of 1-bromo-2-phenyl-2-propanol (2-H) and 1-bromo-2-phenyl-2-propanol hydroperoxide (3-H), together with unreacted 1-H. At temperatures above $250\,^\circ C$ as used for gas chromatographic (GC) analysis, 3-H and part of 2-H are converted into a mixture of acetophenone (4-H), 1-bromo-2-phenylpropene (5-H) and 3-bromo-2-phenylpropene (6-H).

It has been shown (see below) that in the presence of other *para*-substituted α-methylstyrenes (1-Y) the total yields of 2-H, 4-H, 5-H and 6-H derived from reacted 1-H were close to quantitative ($97\cdot4$–100%; cf. Table 1). Obviously, the success of our approach depended on the fact that the product of the measured bromine-atom addition step of the radical-chain reaction, i.e. adduct 7-Y, was immediately trapped by O_2 to give another radical intermediate, the peroxy radical 8-Y, as shown by the equations

$$(5)$$

$$(6)$$
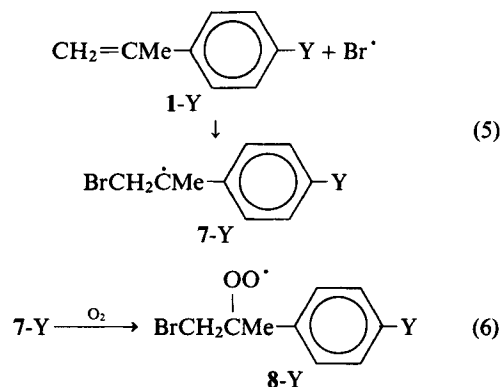
We believe that the interception of radical intermediates

by O_2 (cf. Ref. 10) may turn out to be a useful tool in the study of structure–reactivity correlations of radical reactions.

EXPERIMENTAL

Apparatus. ^1H NMR spectra were obtained at 60 MHz on a Varian EM-360A spectrometer with TMS as the external standard. Mass spectrometry (MS) was carried out using a Finnigen-Mat 4510 GC–MS system. IR spectra were recorded on a Shimadzu IR-440 spectrometer. GC analysis were performed on a Model 103G gas chromatograph equipped with an HP 3390A integrator. An SE-30 capillary column (40 m × 0·2 mm i.d.) was used with a flame ionization detector and with nitrogen as the carrier gas.

Reagents and substrates. THF was dried with LiAlH$_4$ under a nitrogen atmosphere and distilled prior to use. α-Methylstyrene was purchased from Tokoi Kasei and used as received. As reported in Ref. 11, gaseous HBr was generated by reaction of Br$_2$ with tetralin and the unreacted Br$_2$ was removed by passage through a trap cooled at $-70\,°C$. DBPO was used in the form of a 0·2 M solution in hexane kept at $-20\,°C.^{12}$

Substituted α-methylstyrenes, 1-Y with Y = Me, SMe, OMe, F, Cl and Br, were prepared by previously reported methods.^{13,14} Compound 1-CF$_3$ was obtained by dehydration (4 Å molecular sieve as catalyst, 250 °C) of 2-(4'-trifluoromethylphenyl)propen-2-ol. Compound 1-COMe was prepared by dehydration of 2-(4'-acetylphenyl)propan-2-ol (K$_2$S$_2$O$_7$ as catalyst, 200 °C). This propanol was obtained from the reaction of the ethylene glycol ketal of p-acetylphenyl magnesium bromide and acetone followed by hydrolysis in a refluxing mixture of acetone and 10% HCl. The substituted α-methylstyrenes 1-Y with Y = COOMe, CN and NO$_2$ were prepared from the corresponding isopropylbenzenes via two consecutive steps of bromination with N-bromosuccinimide and HBr elimination.^{15} All 1-Y substrates are known compounds and were further identified by ^1H NMR and IR spectroscopy. Boiling or melting points of 1-Y prepared in our laboratory were as follows: 1-CF$_3$, 124–126 °C/45 Torr;^{16} 1-NO$_2$, 120–125 °C/4 Torr (lit.^{15} 106–107 °C/1·2 Torr); 1-CN, 135–140 °C/40 Torr (lit.^{14} 87 °C/20 Torr); 1-Cl, 98–100 °C/25 Torr (lit.^{14} 88–89 °C/15 Torr); 1-F, 98 °C/90 Torr (lit.^{14} 97–101·5 °C/95 Torr); 1-Br, 118 °C/25 Torr (lit.^{14} 114·5–117·5 °C/24 Torr); 1-COOMe, 128–130 °C/12 Torr, m.p. 51–52 °C (lit.^{17} 51–52 °C); 1-Me, 102–103 °C/50 Torr (lit.^{13} 187 °C/760 Torr); 1-COMe, 125–126 °C/10 Torr (lit.^{18} 65–70 °C/0·4 Torr); 1-MeO, 126–128 °C/35 Torr (lit.^{14} 63–65·5 °C/0·5 Torr); 1-SMe, 138–140 °C/21 Torr (lit.^{19} 85 °C/1 Torr).

Reaction of 1-H in HBr–THF–O$_2$–DBPO system. In a round-bottomed flask (100 ml), a mixture of THF (20 ml), 1-H (10 mmol), internal GC standards (100 μl), 0·2 M DBPO solution in hexane (1 ml, 2 mol%) were mixed. The flask was immersed in a thermostated bath (30·0 ± 0·5 °C) and vigorously stirred. A stream of O$_2$ (10 ml min^{-1}) carrying gaseous HBr was passed through the solution.^{20} The approximate concentration of HBr in the solution was monitored by observing the pH of a mixture of the THF solution and a roughly equal amount of water. The pH value was maintained at 2–4 by controlling the rate of HBr generation. After 1 h, TLC analysis of the crude product indicated the presence of two products, the bromohydrin 2-H and the bromohydroperoxide 3-H. Both are known compounds and were identified by ^1H NMR spectroscopy: 2-H, δ 1·50 (3H, CH$_3$, s), 2·6 (1H, OH, s), 3·50 (2H, CH$_2$Br, s), 7·5 (5H, H on benzene ring, s); 3-H,^{15} δ 1·53 (3H, CH$_3$, s), 3·6 (2H, CH$_2$Br, s), 7·2 (5H, s), 8·5 (1H, OOH, s). ^1H NMR also showed that the relative amounts of 2-H and 3-H were roughly 3:2. On distillation, the hydroperoxide 3-H decomposes into 4-H (bath at 120 °C, at 2 Torr). This was indicated by the disappearance of the ^1H NMR signals of 3-H and the appearance of the signals of 4-H [δ 2·4 (3H, CH$_3$, s), 7·2 (5H, m)].

However, when the crude reaction solution was analysed by GC, five compounds, i.e. 1-H, 2-H, 4-H, 5-H and 6-H, were detected. By comparison with authentic samples, their yields were found to be 1-H 34·0%, 2-H 31·3%, 4-H 20·0%, 5-H 4% and 6-H 7·7% (total yield 97%). This result indicates that the bromohydrin 2 will decompose at the vaporization temperature of 350 °C of GC analysis to yield 5-H and 6-H. This was further established by independent experiments on the thermal decomposition of authentic samples of 2-H as described below.

An authentic sample of 2-H needed for GC and NMR analysis was prepared according to Ref. 21. GC analysis of a pure sample of 2-H with a vaporization temperature above 300 °C was found to yield a mixture of 2-H, 5-H and 6-H. Preparative GC (vaporization temperature 350 °C, 3 m × 5 mm i.d. column packed with 15% SE-30 on 60–80-mesh Chromosorb 102 at 200 °C) of 2-H yielded a 4:1 mixture of 5-H and 6-H. The mixture of 5-H and 6-H could not be further separated by preparative GC, although they were separable by high-performance capillary GC. The mixture of 5-H and 6-H was then identified by NMR and MS. ^1H NMR (CCl$_4$), δ 1·1 (0·6H, s), 4·2 (1·6H, s), 6·3 (0·2H, s), 7·3 (5H, m) ppm. GC–MS, m/z (relative intensity, %): 5-H, 198 (M$^+$ + 2, 94), 196 (100), 177 (91), 115 (87), 102 (29); 6-H, 198 (M$^+$ + 2, 51), 196 (54), 117 (100), 115 (95), 91 (29).

Kinetic competition procedure. In a round-bottomed flask (100 ml), a solution of 1-Y (4–5 mmol), 1-H

(5 mmol), internal GC standards (100 μl each) and 0.2 M DBPO solution in hexane (1 ml) in THF (20 ml) was added and vigorously stirred at 30.0 $\pm$ 0.05 °C. A stream of O_2 (10 ml min^{-1}) carrying gaseous HBr was passed through the solution. The concentration of HBr in the solution was controlled as described above. After 30–60 min, the degree of conversion of 1-H or 1-Y could reach 55% ($\varphi = 0.45$) to 98% ($\varphi = 0.02$). During this time, 15–20 samples (about 0.1 ml each) were taken at 3–5 min time intervals, and immediately injected into cooled tubes containing 1–2 mg of NaHCO$_3$ and 1–2 mg of hydroquinone, which were then sealed and the contents subsequently analysed by GC. Typical GC conditions were oven temperature 350 °C, column temperature increased from 80 to 220 °C at 10 °C min^{-1} and carrier gas flow-rate 3 ml min^{-1}.

GC internal standards were chosen according to the requirements of convenient retention times and no interference with the integration of the substrate and product GC peak. The internal standards used were decane for 1-H and 1-F, undecane for 1-CF$_3$ and 1-Me, dodecane for 1-CN, 1-Cl, 1-Br, 1-COMe and 1-OMe and pentadecane for 1-NO$_2$, 1-CO$_2$Me and 1-SMe.

The total yields of bromo–oxygen adducts were almost quantitative during competitive runs when 1-H was mixed with different 1-Y (Y = CF$_3$, Cl, OMe, CN, COOMe and SMe) as indicated in Table 1.

The fact that all products (2-H to 6-H) are formed from the same irreversible elementary step [equation (5)] ensures the applicability of equation (7):[22]

$$k_r(Y) = \frac{k_Y}{k_H} = \frac{\log\{[1\text{-}Y]_t/[1\text{-}Y]_0\}}{\log\{[1\text{-}H]_t/[1\text{-}H]_0\}} = \frac{\log \varphi_Y}{\log \varphi_H} \quad (7)$$

in which φ is defined as the mole fraction of unreacted substrate, i.e. $[1]_t/[1]_0$, for the calculation of relative rate constants $k_r(Y)$. As the GC peaks of 1-F and 1-H overlap with each other, $k_r(F)$ cannot be measured by direct competition between 1-F and 1-H. However, direct competition between 1-F and 1-Me is experimen-

Table 1. Yields of the reaction products of 1-H in the THF–O$_2$–HBr–DBPO system in the presence of various 1-Y[a]

Y	t (min)	1-H	2	4	5 + 6	Total
—	60	34	31.3	20.0	11.7	97
CF$_3$	78	10.5	<1	88	<1	98.5
Cl	82	22	46.7	19.9	9.2	97.8
OMe	82	39	34	19.4	5	97.4
CN	30	54.3	22.4	19.8	3.9	100.0
COOMe	66	10.6	51.0	20.2	7.7	98.7
SMe	50	58.6	38.4	15.8	6.0	98.8

[a] Obtained from GC analysis calibrated with authentic samples.

Table 2. Relative reactivity of 1-Y with respect 1-H [k_r(Y) values] measured in the THF–O$_2$–HBr–DBPO system at 30 °C

No.	Y$_1$/Y$_2$	k_r	n	r
1	CF$_3$/H	0.744 $\pm$ 0.010	12	0.9996
2	NO$_2$/H	0.891 $\pm$ 0.009	7	0.9960
3	F/Me	0.795 $\pm$ 0.009	14	0.9992
	F/H[a]	0.916 $\pm$ 0.018		
4	CN/H	0.964 $\pm$ 0.016	6	0.9991
5	Cl/H	1.057 $\pm$ 0.014	10	0.9993
6	Br/H	1.054 $\pm$ 0.018	11	0.9987
7	CO$_2$Me/H	1.072 $\pm$ 0.015	9	0.9993
8	Me/H	1.152 $\pm$ 0.019	8	0.9994
9	COMe/H	1.257 $\pm$ 0.026	8	0.9988
10	OMe/H	1.508 $\pm$ 0.013	10	0.9994
11	SMe/H	1.789 $\pm$ 0.039	9	0.9980

[a] $k_F/k_H = (k_F/k_{Me})(k_{Me}/k_H) = 0.916$

tally feasible, hence the k_r(F) value in Table 2 was calculated using the equation $k_F/k_H = (k_F/k_{Me})(k_{Me}/k_H)$.

According to equation (7), if a set of φ values (1.0–0.2) were measured over a wide range of reaction times which correspond to a wide range of the extent of reaction (0–80%) at different conversions of 1, then a linear relationship of ln φ_Y (time t) with ln φ_H (time t) would be obtained if all the products were derived from the same rate-limiting step and if the adopted kinetic methodology were reliable.

In fact, we obtained 11 excellent linear plots [see correlation coefficient (r) values in Table 2] on the basis of 11 sets of ln φ_Y vs ln φ_H plots with φ value falling mainly in the range 1.0–0.2. These 11 sets correspond, of course, to 11 pairings of 1-Y with 1-H. A typical example is illustrated in Figure 1 for the kinetic com-
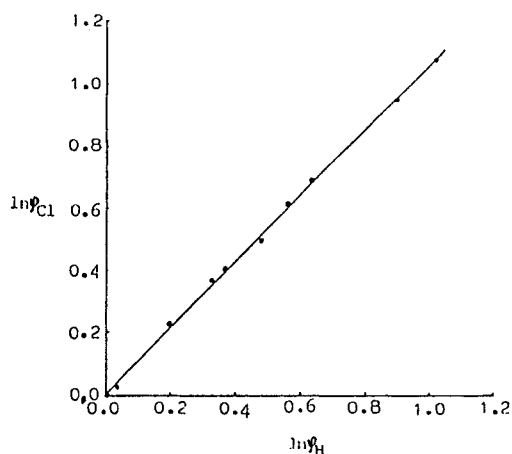

Figure 1. Plot of ln φ_{Cl} vs ln φ_H

Table 3. φ Values of the reaction of 1-Cl and 1-H in competition for the bromine atoms at ten successive time intervals

t (min)	φ_H	$-\text{Ln } \varphi_H$	φ_{Cl}	$-\text{Ln } \varphi_{Cl}$
5	1·00	0	1·00	0
10	0·966	0·034	0·975	0·025
18	0·822	0·197	0·795	0·229
26	0·712	0·331	0·691	0·370
30	0·690	0·371	0·668	0·404
34	0·616	0·485	0·610	0·495
42	0·568	0·566	0·539	0·618
46	0·527	0·640	0·503	0·688
54	0·406	0·901	0·386	0·953
58	0·359	1·024	0·338	1·085

Table 4. Measurement of $k_r(Cl)$ values at different molar ratios of 1-H and 1-Cl

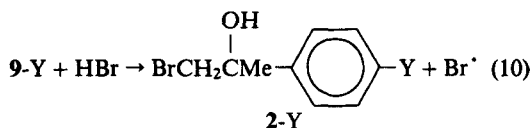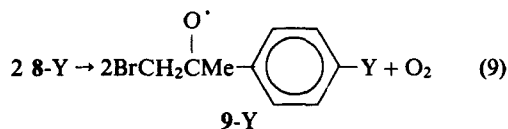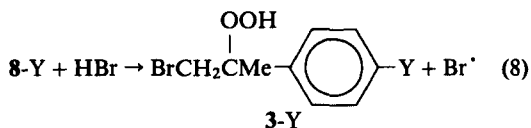| 1-H (mmol)	1-Cl (mmol)	k_r (Cl)	n	r
6·04	1·27	1·04 ± 0·03	9	0·997
4·85	4·22	1·057 ± 0·014	10	0·9993
0·92	3·49	1·07 ± 0·03	6	0·996

petition between 1-Cl and 1-H, with the corresponding φ and $\ln \varphi$ values listed in Table 3. Table 2 shows that the $k_r(Cl)$ value from the regression analysis is $1·057 \pm 0·014$ with $r = 0·9993$. The $k_r(Y)$ values summarized in Table 2 are the averaged $k_r(Y)$ values obtained from regression analysis[28] of the 6–14 independently measured k_r values at 6–14 consecutive time intervals. The number of these measurements is designated as n in Table 2 and is illustrated by the ten points in Figure 1. These $k_r(Y)$ values are almost the same as all the $k_r(Y)$ values obtained by simply averaging the n independently measured k_r values. These results demonstrate that the chosen reaction fulfils our proposed requirements and that the adopted kinetic methods are truly reliable.

Before systematic evaluation of the eleven $k_r(Y)$ values by the standard procedure described above with the molar ratio of the reactants 1-H and 1-Y fixed at 1 : 1, the reliability of the methodology was further cross-checked by measuring the $k_r(Cl)$ values at different molar ratios of 1-Cl and 1-H. The results are summarized in Table 4, which shows that within experimental uncertainty the $k_r(Cl)$ values are not affected by either the reactant molar ratios (cf. Table 4) or the degree of conversion of the 1-Y substrates (cf. Table 3 and Figure 1).

DISCUSSION

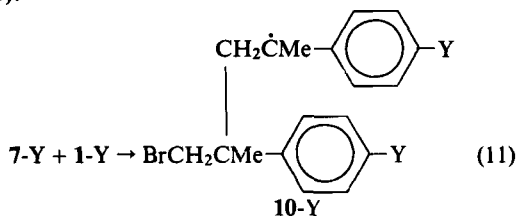The radical chain reaction paths initiated by a bromine-atom addition to olefins [equation (5)] in the presence of O_2 and HBr [equations (6), (8) and (10)] have been well documented[20] and can be summarized by the equations (5), (6), (8), (9) and (10):

$$8\text{-Y} + \text{HBr} \rightarrow \text{BrCH}_2\text{CMe}\!\!\left(\!\overset{\overset{\displaystyle \text{OOH}}{|}}{\bigcirc}\!\right)\!\!-\text{Y} + \text{Br}^\cdot \quad (8)$$
$$\text{3-Y}$$

$$2\ 8\text{-Y} \rightarrow 2\text{BrCH}_2\text{CMe}\!\!\left(\!\overset{\overset{\displaystyle \text{O}^\cdot}{|}}{\bigcirc}\!\right)\!\!-\text{Y} + O_2 \quad (9)$$
$$\text{9-Y}$$

$$9\text{-Y} + \text{HBr} \rightarrow \text{BrCH}_2\text{CMe}\!\!\left(\!\overset{\overset{\displaystyle \text{OH}}{|}}{\bigcirc}\!\right)\!\!-\text{Y} + \text{Br}^\cdot \quad (10)$$
$$\text{2-Y}$$

Clearly, Br$^\cdot$ radicals are generated from HBr by chain steps such as equations (8) and (10), they then add to 1-Y to give the intermediate radical 7-Y [equation (5)], which is subsequently trapped by O_2 to give the peroxy radical 8-Y [equation (6)]. Compound 8-Y can either abstract an H atom from HBr to give the peroxide 3-Y [equation (8)] or disproportionate into the oxy radical 9-Y [equation (9)], which regenerates another Br$^\cdot$ by abstracting an H atom from HBr to form the hydroxy-bromo adduct 2-Y [equation (10)].
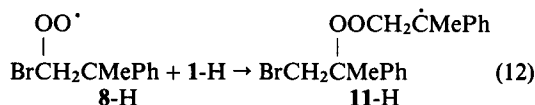
Under our experimental conditions, the concentration of O_2 was ca $0·02$ M at $30\,°C$ in THF,[24] if $[1] = 0·5$ M and the HBr concentration was $>10^{-4}$ M, and other possible side-reactions most probably could not compete with the main reactions [equations (5), (6), (8), (9) and (10)] described above on account of the following considerations.

1. Fast trapping of 7 by O_2 (cf. Ref. 25, the trapping rate of tBu$^\cdot$ by O_2 is 5×10^9 l mol^{-1}s^{-1} at $25\,°C$) would easily suppress the telomerization of 1-Y [equation (11)] (cf. Ref. 26a; e.g. the propagation rate of $CH_2{=}CMe_2$ polymerization is only 50 l mol^{-1}s^{-1} at $60\,°C$).

$$7\text{-Y} + 1\text{-Y} \rightarrow \text{BrCH}_2\text{CMe}\!\!\left(\!\bigcirc\!\right)\!\!-\text{Y} \quad (11)$$
$$\text{10-Y}$$

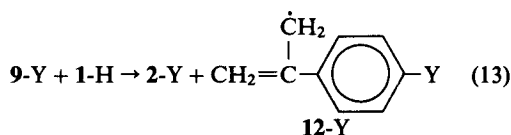with upper fragment: $CH_2\overset{\cdot}{C}Me\!\!\left(\!\bigcirc\!\right)\!\!-\text{Y}$

2. High rate of chain-transfer between 8-Y and HBr [equation (8)] {cf. Ref. 27, the reaction rate of iPrOO$^\cdot$ and HBr in the gas phase is calculated to be of the order of 10^6 l mol^{-1}s^{-1} at $30\,°C$ from the log A ($10·8$ l mol^{-1}) and E_a [$6·5$ kcal mol^{-1}

(1 kcal = 4·184 kJ)] values} would effectively suppress the formation of peroxidic radicals such as 11-Y [equation (12) [[cf. Ref. 26b; for equation (12) with 8-H, $k = 2·85\ 1\,mol^{-1}\,s^{-1}$ at 30 °C)].

$$
\begin{array}{ccc}
OO^{\cdot} & & OOCH_2\dot{C}MePh \\
| & & | \\
BrCH_2CMePh + 1\text{-}H \rightarrow & BrCH_2CMePh & \quad (12) \\
\text{8-H} & & \text{11-H}
\end{array}
$$

3. The fast H-abstraction by 9-Y from HBr [cf. Ref. 28; the H-abstraction rate from HBr by tBuO$^{\cdot}$ can be estimated to be of the order of 10^9–$10^{10}\ 1\,mol^{-1}\,s^{-1}$ at 30 °C from the estimated A ($10^{9-10}\ 1\,mol^{-1}\,s^{-1}$) and E_a (0–2 kcal mol^{-1}) values[28]] would easily suppress the H-abstraction by 9 from 1-Y [equation (13)] (cf. Ref. 26c; the H-abstraction rate of tBuO$^{\cdot}$ from propene is $10^{4\cdot4}\ 1\,mol^{-1}\,s^{-1}$ at 30 °C).

$$
9\text{-}Y + 1\text{-}H \rightarrow 2\text{-}Y + CH_2{=}C\underset{\text{12-Y}}{\overset{\dot{C}H_2}{\vert}}\!\!\!\!\!\!\!\!\!\!\!\!\bigcirc\!\!{-}Y \quad (13)
$$

It is known that the Br$^{\cdot}$ addition to olefins is reversible,[29] e.g. the equilibrium constant of Br$^{\cdot}$ addition to ethylene can be calculated to be only 10 1 mol^{-1} at 30 °C [equation (14)] ($\Delta H = -8·8$ kcal mol^{-1}, $\Delta S = -24·0$ cal mol^{-1} K^{-1}; cf. Ref. 30).

$$
CH_2{=}CH_2 + Br^{\cdot} \rightleftharpoons \underset{\text{13}}{BrCH_2\dot{C}H_2} \quad (14)
$$
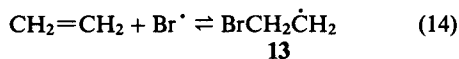
However, Br$^{\cdot}$ addition to 1 will yield a relatively stable radical 7 because the stablization energy of 7 might be more than 10 kcal mol^{-1} greater than that of 13 (the stablization energy of Et is $-0·5$ kcal mol^{-1} and that of benzyl is 11·6 kcal mol^{-1}; cf. Ref. 31), and the enthalpy (ΔH) of equation (5) could thus be estimated to be less than -19 kcal mol^{-1}. If the entropic terms for the two reactions do not differ greatly, the equilibrium constant of equation (5) could be estimated to be larger than 10^8 1 mol^{-1} at 30 °C. On the other hand, the rate constant for the same Br$^{\cdot}$ addition step [equation (5)] can be roughly estimated to be of the order of 10^6–10^8 1 mol^{-1} s^{-1} {By using isobutene as an approximate model for styrene, the rate constant for the Br$^{\cdot}$ addition step [equation (5)] can be roughly estimated to be of the order of 10^6–10^8 1 mol^{-1} s^{-1} by considering the following facts: (1) the rate constant of a radical reaction in solution can be several orders of magnitude slower than that of the same reaction in the gas phase, e.g. the rate constant of the primary H-abstraction from isobutane by Cl$^{\cdot}$ in the gas phase is $3·2 \times 10^{10}$ 1 mol^{-1} s^{-1}, but is only $2·2 \times 10^6$ 1 mol^{-1} s^{-1} in benzene;[32] (2) the rate constant of the Br$^{\cdot}$ addition to ethylene is $10^{6\cdot96}$ 1 mol^{-1} s^{-1} at 25 °C in the gas phase,[30] but the rate-constant ratio of Br$^{\cdot}$ addition to isobutene and ethylene is 384 in the gas phase, hence the

rate constant of Br$^{\cdot}$ addition to isobutene might be $384 \times 10^{6\cdot96} = 3·5 \times 10^9$ 1 mol^{-1} s^{-1} in the gas phase, but probably 10^6–10^8 1 mol^{-1} s^{-1} in the liquid phase.}. Thus the rate-constant for the reverse reaction of equation (5) is very probably $0·01$–1 s^{-1}. Certainly, if this reaction [equation (5)] is intercepted by the exceedingly fast reaction with O$_2$ [equation (6)] it will have very little chance of reversal. The irreversibility of the measured reaction [equation (5)] guaranteed that requirements (ii) and (iii) (cf. fourth paragraph of the Introduction) were fulfilled, and that a truly rigorous kinetic procedure could be worked out, as in requirement (iv).

As described above and summarized in Table 2, our methodology has provided a reliable set of $k_r(Y)$ values for 11 substituents. These k_r values are not affected by the degree of conversion of the substrates. The precision of the k_r measurements is clearly reflected in the r value in Table 2.

Clearly, we are now in a position to make a correlation analysis of our data. Values of σ^* and σ^x were taken from the following sources: σ^*_{JJ}, Ref. 1; σ^*_α, Ref. 4b; σ^*_C, Ref. 4d; σ^*_F, Ref. 33; σ^*_J and RRS, Ref. 3; σ_p and σ^+, Ref. 2c; and σ_{mb}, Ref. 8. Correlations of our data with both equations (1) and (2) are summarized in Table 5, in which R, ψ, F, ρ^x and ρ^* values are listed.

A plot of these log k_r values versus σ^x, i.e. σ_p, σ^+ and σ_{mb}, is shown in Figure 2. Both the scatter of points in Figure 2 and the R and ψ values (0·760 and 0·718; 0·646 and 0·844; 0·591 and 0·892) calculated on the basis of the single-parameter equation (2) indicate no meaningful correlation between k_r and σ^x. Even if we use dual-parameter correlations with two different polar σ^x values, i.e., $\rho^1\sigma^{x1} + \rho^2\sigma^{x2}$, the correlation cannot be greatly improved. For instance, the 'best pair,' i.e., $\sigma^+ + \sigma_{mb}$ with $n = 11$, yields a correlation coefficient of only 0·899, whereas four of the R values of the dual-parameter correlations (cf. Table 5) are greater than 0·99.

Application of the dual-parameter equation (1) with various combinations of σ^x and σ^*, however, completely changes the picture. The correlation is greatly improved by using the dual-parameter equation instead of the single-parameter equation. As summarized in Table 5, all possible combinations of σ^x and σ^* had been tried, with $\sigma^x = \sigma_p$, σ^+ and σ_{mb}, and $\sigma^* = \sigma^*_{JJ}$, σ^*_α, σ^*_C, σ^*_F, σ^*_J and RRS. Only meaningful correlations are summarized in Table 5. Evidently, on the basis of the R, ψ and F values, the $\sigma^*_{JJ} + \sigma_{mb}$ combination gives the best correlation ($R = 0·997$, $\psi = 0·086$ and $F = 739$). This is expected because the σ^*_{JJ} is the most self-consistent and cross-checked σ^* scale and the σ_{mb} scale is tailor-made for the reactivity of the double bond of substituted styrenes.[1,8,9] In Figure 3, experimental log k_r values are plotted against calculated values based on this correlation. The results clearly show that within experimental uncertainty, all points fall on the line.

Table 5. Values of ρ^x and ρ^* of equations (1) and (2) and corresponding values of the correlation
coefficient R, Ψ^{2b} and F-test[31] for correlation of $k_r(Y)$ values of n 1-Ys with σ^x and σ^{*a}

σ^x or $\sigma^x + \sigma^*$		ρ^x	ρ^*	n	R	Ψ	F^b
	σ^+	$-0\cdot152 \pm 0\cdot046$		11	$0\cdot743$	$0\cdot74$	11
	σ_p	$-0\cdot191 \pm 0\cdot081$		11	$0\cdot619$	$0\cdot87$	$5\cdot6$
	σ_{mb}	$-0\cdot119 \pm 0\cdot057$		11	$0\cdot570$	$0\cdot91$	$4\cdot3$
σ_{JJ}^*	σ^+	$-0\cdot156 \pm 0\cdot009$	$0\cdot347 \pm 0\cdot024$	11	$0\cdot992$	$0\cdot15$	237
σ_{JJ}^*	σ_p	$-0\cdot241 \pm 0\cdot014$	$0\cdot419 \pm 0\cdot024$	11	$0\cdot992$	$0\cdot15$	252
σ_{JJ}^*	σ_{mb}	$-0\cdot168 \pm 0\cdot006$	$0\cdot449 \pm 0\cdot014$	11	$0\cdot997$	$0\cdot09$	740
σ_α^*	σ^+	$-0\cdot160 \pm 0\cdot011$	$2\cdot87 \pm 0\cdot02$	9	$0\cdot992$	$0\cdot16$	169
σ_α^*	σ_p	$-0\cdot251 \pm 0\cdot030$	$3\cdot36 \pm 0\cdot04$	9	$0\cdot978$	$0\cdot25$	66
σ_α^*	σ_{mb}	$-0\cdot143 \pm 0\cdot016$	$3\cdot09 \pm 0\cdot03$	9	$0\cdot986$	$0\cdot20$	104
σ_C^*	σ^+	$-0\cdot187 \pm 0\cdot019$	$0\cdot347 \pm 0\cdot053$	9	$0\cdot979$	$0\cdot25$	66
σ_C^*	σ_p	$-0\cdot303 \pm 0\cdot037$	$0\cdot434 \pm 0\cdot066$	9	$0\cdot970$	$0\cdot30$	43
σ_C^*	σ_{mb}	$-0\cdot169 \pm 0\cdot028$	$0\cdot415 \pm 0\cdot077$	9	$0\cdot960$	$0\cdot34$	35
σ_F^*	σ^+	$-0\cdot143 \pm 0\cdot076$	$0\cdot140 \pm 0\cdot193$	8	$0\cdot718$	$0\cdot92$	$2\cdot1$
RRS	σ^+	$-0\cdot175 \pm 0\cdot018$	$0\cdot015 \pm 0\cdot002$	11	$0\cdot970$	$0\cdot30$	58
RRS	σ_p	$-0\cdot280 \pm 0\cdot028$	$0\cdot019 \pm 0\cdot002$	11	$0\cdot971$	$0\cdot29$	60
RRS	σ_{mb}	$-0\cdot159 \pm 0\cdot024$	$0\cdot017 \pm 0\cdot003$	11	$0\cdot954$	$0\cdot35$	40

[a] When $n = 11$, Y = CF₃, NO₂, F, CN, Cl, Br, CO₂Me, Me, COMe, OMe and SMe. When $n = 9$, for σ_α^*, Y = CF₃, F, CN,
Cl, CO₂Me, Me, COMe, OMe and SMe; for σ_C^*, Y = CF₃, F, CN, Cl, Br, CO₂Me, Me, OMe and SMe; for σ_F^*, Y = NO₂,
F, CN, Cl, Br, Me, COMe, OMe and SMe.
[b] Critical F values: $F_{0\cdot001(1,9)} = 22\cdot9$, $F_{0\cdot01(1,9)} = 10\cdot6$, $F_{0\cdot001(2,8)} = 18\cdot5$, $F_{0\cdot001(2,6)} = 27\cdot0$, $F_{0\cdot01(2,8)} = 8\cdot7$, $F_{0\cdot01(2,6)} = 10\cdot9$,
$F_{0\cdot001(2,5)} = 37\cdot1$, $F_{0\cdot01(2,5)} = 13\cdot3$.
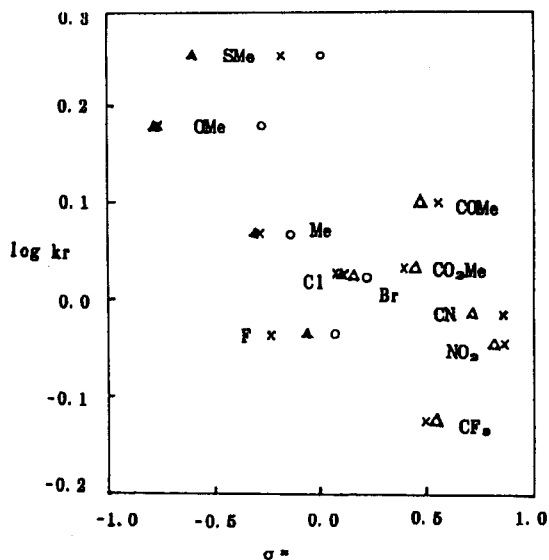
Figure 2. Plot of log k_r vs σ^x: (▲) σ^+; (○) σ_p; (×) σ_{mb}
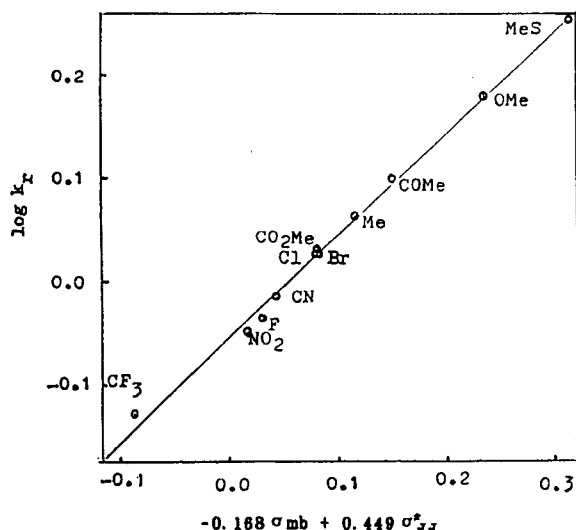
Figure 3. Plot of experimental log k_r values vs values
calculated by $-0\cdot168\sigma_{mb} + 0\cdot449\sigma_{JJ}^*$

A $|\rho^x/\rho^*|$ ratio can be calculated from any pair of ρ^x and ρ^* listed in Table 5. The $|\rho^x/\rho_{JJ}^*|$ ratio is based on the arbitrary definition that ρ^* is equal to unity for the σ_{JJ}^* scale,[1] and therefore the absolute magnitude of the $|\rho^x/\rho_{JJ}^*|$ ratio or any $|\rho^x/\rho^*|$ ratio has no physical meaning, but the relative values of a series of $|\rho^x/\rho^*|$ ratios using the same σ^x and σ^* scales have a meaning, i.e. a larger $|\rho^x/\rho^*|$ value signifies a larger polar contribution.[1] It is noteworthy that the $|\rho_{mb}/\rho_{JJ}^*|$ ratios for the three accurately measured radical addition reactions are comparable in magnitude, i.e. 0·37 for the present work, 0·42 for trichloromethyl radical addi-

tion[8] and $0 \cdot 30$ for the cyclodimerization of α,β,β-trifluorostyrenes.[1] Evidently, both polar and spin-delocalization effects play important roles in the TSs of these three radical additions. Further, the ρ values in this work, i.e. $-0 \cdot 168$ for ρ_{mb} and $0 \cdot 449$ for ρ_{JJ}^*, are much larger than their calculated deviations, i.e. $0 \cdot 006$ for ρ_{mb} and $0 \cdot 014$ for ρ_{JJ}^*.

In conclusion, in radical addition reactions with TSs in which π-bonds are partially broken, the relative rate constants should be correlated by the dual-parameter equation (1) if steric effects are negligible. Various possible combinations of $\sigma^x + \sigma^*$ should be compared in order to find out which σ^* scale is the most reliable. Both this work and parallel work[8] show that the $\sigma_{JJ}^* + \sigma_{mb}$ combination leads to the best correlation for additions to styrenes.

ACKNOWLEDGEMENT

REFERENCES

1. X. K. Jiang and G. Z. Ji, *J. Org. Chem.* **57**, 6051 (1992), and references cited therein.
2. (a) L. P. Hammitt, *Physical Organic Chemistry*, 2nd ed., Chapt. 11. McGraw-Hill, New York (1970); (b) J. Shorter, *Correlation Analysis of Organic Reactivity*, Wiley, Chichester (1982); (c) O. Exner, *Correlation Analysis of Chemical Data*, p. 61, Plenum Press, New York (1988); (d) R. W. Taft and R. D. Topsom, *Prog. Phys. Org. Chem.* **16**, 1 (1987); (e) C. Hansch, A. Leo and R. W. Taft, *Chem Rev.* **91**, 165 (1991).
3. H. G. Viehe, Z. Janousek and R. Merenyi (Eds), *Substitent Effects in Radical Chemistry*, Reidel, Dordrecht (1986).
4. (a) R. L. Huang, S. H. Goh and S. H. Ong, *The Chemistry of Free Radicals*, Chapt. 9 and pp. 31–39. Arnold, London (1974); (b) E. Baciocchi, B. Giese, H. Fashchi and R. Ruzziconi, *J. Org. Chem.* **55**, 5688 (1990); (c) S. S. Kim, C. S. Lee, C. C. Kim and H. J. Kim. *J. Phys. Org. Chem.* **3**, 803 (1990); (d) X. Creary, in Ref. 3. p. 245; (e) O. Ito and M. Matsuda, *J. Org. Chem.* **47**, 2261 (1982); (f) C. M. M. Da Silva Correa, M. D. C. M. Fleming and M. A. B. C. S. Oliveira, in *Free Radicals in Synthesis and Biology*, edited by J. Minisci, pp. 317–324, Kluwer, Dordrecht (1988); (g) F. Lahouse, R. Merenyi, J. R. Desmuts, H. Allaime, A. Borghese and H. G. Viehe, *Tetrahedron Lett.* **25**, 3823 (1984); (h) D. C. Nonhebel and J. C. Walton, *Free Radical Chemistry*, pp. 178–179. Cambridge University Press, Cambridge (1974).
5. (a) J. B. Afanasev, *Russ. Chem. Rev.* **40**, 216 (1971); (b) X. K. Jiang, G. Z. Ji and C. X. Yu, *Acta Chim. Sin.* **42**, 599 (1984); *Engl. Ed.* **82** (1984); (c) R. Merenyi, Z. Janonsek and H. G. Viehe, in Ref. 3, pp. 301–324; (d) S. Dincturk, R. A. Jackson, H. Townson, H. Agirbas, N. C. Billingham and G. J. March, *J. Chem. Soc., Perkin Trans. 2* 1121 (1981); (e) T. H. Fisher, S. M. Dershem and M. L. Prewitt, *J. Org. Chem.* **55**, 1040 (1990); (f) A. D. Jenkins, in *Advances in Free-Radical Chemistry*, edited by G. H. Williams, pp. 139–201, Logos Press, London (1967); (g) H. Sakurai, S.-I. Huyashi and A. Hosomi, *Bull. Chem. Soc. Jpn.* **44**, 1945 (1971); (h) T. Yamamoto and T. Otsu, *J. Polym. Sci., Part A* 1279 (1969); (i) R. Ito, T. Migita, N. Morikawa and O. Simamura, *Tetrahedron* **21**, 955 (1965).
6. J. M. Dust and D. R. Arnold, *J. Am. Chem. Soc.* **105**, 1221 (1983).
7. (a) X. K. Jiang, G. Z. Ji and C. X. Yu, *Acta Chim. Sin.* **44**, 72 (1986); *Engl. Ed.* 369 (1985); (b) G. Z. Ji, X. K. Jiang and W. T. Shi, *Chin. J. Chem.* **9**, 521 (1991).
8. G. H. Guo, S. S. Sun, G. Z. Ji and X. K. Jiang, *J. Chem. Res. (S)* 166 (1993); *J. Chem. Res. (M)* 1123 (1993).
9. G. Z. Ji, X. K. Jiang, Y. Z. Zhang, S. G. Yuan, X. C. Yu, Y. Q. Shi, X. L. Zhang and W. T. Shi, *J. Phys. Org. Chem.* **3**, 643 (1990).
10. X. K. Jiang, T. F. Xu and J. Wu, *Acta Chim. Sin., Engl. Ed* 285 (1989).
11. H. S. Booth, *Inorganic Synthesis*, Vol. I, p. 151, McGraw-Hill, New York (1939).
12. P. D. Bartlett, E. P. Bening and R. E. Pincock, *J. Am. Chem. Soc.* **82**, 1762 (1960).
13. W. H. Perkin and S. S. Pickels, *J. Chem. Soc. Trans.* **87**, 639 (1905).
14. L. C. King, R. M. Dodson and L. A. Sublusky, *J. Am. Chem. Soc.* **70**, 1178 (1948).
15. (a) W. H. Richardson and D. L. Siggall-Estbery, *J. Am. Chem. Soc.* **104**, 4173 (1982); (b) W. H. Richardson, M. B. Deington and H. E. Oneal, *J. Am. Chem. Soc.* **94**, 1619 (1972).
16. R. Popielarz and D. R. Arnold, *J. Am. Chem. Soc.* **112**, 3068 (1990).
17. (a) R. Anet and F. A. Anet, *J. Am. Chem. Soc.* **86**, 525 (1964); (b) J. C. Petropoulos and R. K. Madison, *Chem. Abstr.* **60**, P476f (1964).
18. A. F. Gladkikh, B. A. Zaitsev and G. A. Shtraikhman, *Probl. Organ. Sinteaz, Akad. Nauk SSSR, Otd. Obshck. i Tekhn. Khim.* **118** (1965); *Chem. Abstr.* **64**, 9628g (1966).
19. G. Fraenkel and J. M. Geckel, *J. Am. Chem. Soc.* **102**, 2869 (1980).
20. (a) A. Rieche, M. Schulz and K. Kurschke, *Chem. Ber.* **99**, 3244 (1966); (b) S. Miyajima, S. Ichihara and S. Simamura, *Bull. Chem. Soc. Jpn.* **48**, 531 (1975).
21. C. O. Guss and R. Rosenthall, *J. Am. Chem. Soc.* **77**, 2549 (1955).
22. (a) S. P. Skell and A. Y. Garner, *J. Am. Chem. Soc.* **78**, 5430 (1956); (b) G. A. Russell, in *Investigation of Rates and Mechanisms of Reactions*, edited by S. L. Friess, E. S. Lewis and A. Weissberger, pp. 343–344. Interscience, New York (1961); (c) J. I. G. Cadogan and I. H. Sadler, *J. Chem. Soc. B* 1191 (1966).
23. G. E. Box, W. G. Hunter and J. S. Hunter, *Statistics for Experimenters, an Introduction to Design, Data, Analysis and Model Building*, Wiley, New York (1978).
24. H. Stephen and T. Stephen, *Solubilities of Inorganic and Organic Compounds*, Vol. 1, Part 1, p. 575, Pergamon Press (1963).
25. P. Netu, P. E. Huce and A. B. Ross, *J. Phys. Chem. Ref. Data*, 413 (1990).
26. J. K. Kochi, *Free Radicals*, (a) Vol. 1, p. 86; (b) Vol. 2, p. 28; (c) Vol. 1, p. 74; (d) Vol. 1, p. 28, Wiley–Interscience, New York (1973).

27. J. A. Kerr and S. J. Moss, *Handbook of Bimolecular and Termolecular Gas Reactions*, p. 351, CRC Press, Boca Raton, FL (1987).

28. L. Batt and F. R. Cruickshank, *J. Phys. Chem.* 1836 (1967).

29. D. C. Nonhebel and J. C. Walton, *Free Radicals*, p. 167, Cambridge University Press, Cambridge (1974).

30. J. A. Kerr and M. J. Parsonage, *Evaluation Kinetic Data on Gasphase Addition Reactions*, p. 126, University of Birmingham, Birmingham (1972).

31. (a) D. M. Golden and S. W. Benson, *Chem. Rev.* 125 (1969); (b) Ref. 3, p. 14.

32. (a) R. M. Fristrom, *Rate Constants of Gas Reactions*, p. 91, National Bureau of Standards, Washington, DC (1972); (b) K. U. Ingold, J. Luszyk and K. D. Raner, *Acc. Chem. Res.* 23, 219 (1990).

33. T. H. Fisher and A. W. Meierhoefer, *J. Org. Chem.* 43, 220 (1978).