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Factors Controlling the Addition of Carbon-Centered Radicals to Alkenes

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Summary: The addition rate constants of radicals to alkenes are strongly substituent dependent because of enthalpic, polar and steric effects. Recent absolute experimental and high level ab initio data for many prototype additions of small radicals are analyzed with the aid of the state correlation diagram. This leads to a unifying rationalization of the various effects and allows the prediction of rate constants to one order of magnitude or better. Propagation rate coefficients of homo- and copolymerizations and penultimate effects are also discussed.

Introduction

The addition of carbon-centered radicals to alkenes is the key step of radical polymerizations and of many organic syntheses. The rate constants vary by many orders of magnitude with radical and substrate substitution, and this often determines the success or failure of attempted reactions. Hence, since the early days of radical and polymer chemistry the controlling factors have been intensely discussed, mainly on the basis of relative rate constants, ratios of frequency factors and differences of activation energies. Most additions are exothermic, that is they have negative heats of reaction H_r. Consequently, the transition state (TS) is early and the Evans-Polanyi-Semenov relation $E_a = E_{a0} + \alpha H_r$ predicts that the transition state energy decreases with increasing exothermicity with $\alpha \approx 0.25$. The activation energy is further lowered by so-called polar effects. These represent contributions of charge-transfer (CT) configurations to the TS. Attempts to combine the enthalpy and the polar factors in predictive equations are the Alfrey-Price *Q-e* scheme and the patterns of reactivity schemes of Bamford and Jenkins. In addition, bulky substituents at the attacked carbon atom reduce the rate constants by steric effects.

About two decades ago, important reviews on radical addition reactions were published by Tedder and by Giese.[1] The steric effects were rationalized in terms of Taft's steric constants, and the polar effects were described in terms of the frontier molecular orbital theory and by Hammett substituent constants. Except for phenyl-substituted radicals and alkenes, the enthalpy effects were deemed unimportant, and the radicals were classified as nucleophilic, electrophilic or ambiphilic. Electron-donor-substituted radicals with small ionization energies

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(*IE*) are nucleophilic and react fast with electron-deficient alkenes that have large electron affinities (*EA*). The methyl radical ($\bullet CH_3$) was thought to belong to this class. Acceptor-substituted radicals with large *EA* are electrophilic and react fast with electron-rich alkenes having a low *IE*. Borderline substituted radicals are often ambiphilic, and can react fast with both electron-deficient and electron-rich alkenes. For these, H_r may play a larger role.

In the meantime, considerable progress has been made, both with respect to the availability of precise absolute rate constants and their Arrhenius parameters, and by the development of quantum chemical methods for the calculation of transition states for reasonably-sized systems. The present authors have recently reviewed this progress in detail.[2] Here, we briefly summarize the major conclusions, present the new predictive way of analysis and point to the relevance of the findings for polymerization kinetics. The experimental and theoretical details and all references to original articles are given in the full review.[2]

Experimental Results

Diverse experimental methods of optical spectroscopy and magnetic resonance now allow the direct determination of absolute addition rate constants from time-resolved radical kinetics after a pulsed or intermittent photochemical radical generation. The rate constants range from about 10 $M^{-1}s^{-1}$ nearly to their upper diffusion-controlled limit of about 10^9 $M^{-1}s^{-1}$, and the errors are below 50%. Hitherto, most experiments involved low molecular weight radicals but some monomeric species were also studied. Table 1 displays absolute rate constants at or close to room temperature for the addition of a variety of small radicals to a large series of monosubstituted and 1,1-disubstituted alkenes, including many common monomers. Where available, the decadic logarithms of the frequency factors $\log(A/M^{-1}s^{-1})$ are also given, and the activation energies range from 7.4 to about 40 kJ/mol.

The table includes radicals such as methyl (Me) and benzyl (Bn) that should not exhibit strong polar effects, rather nucleophilic radicals with very small *IE* like hydroxymethyl (MOH), *tert*-butyl (*t*Bu) and 2-hydroxy-2-propyl (POH), and strongly electrophilic radicals with high *EA* such as trifluoroacetonyl (FAc) and a cyclic malonyl radical derived from Meldrum's acid (cMal). According to their *EA* and *IE* the remaining radicals cyanomethyl (MCN), *tert*-butoxycarbonylmethyl (MEst) and their tertiary analogs 2-cyano-2-propyl (PCN) and 2-*tert*-butoxycarbonyl-2-propyl (PEst) are slightly electrophilic or ambiphilic. Data for cumyl, an open-chain malonyl and various other species are also available. The alkenes are ordered according to increasing rate constants for methyl addition with the exception of the styrenes which are placed at the end.

Table 1. Rate constants ($M^{-1}s^{-1}$) at 300°K and logarithmic frequency factors log($A/M^{-1}s^{-1}$) in parentheses.

CH_2=CXY	Radical					
X,Y	non-polar/ nucleophilic	nucleophilic		ambiphilic/ electrophilic		electrophilic
	Me/ Bn	*t*Bu	POH/ MOH	PEst/ PCN	MEst/ MCN	*c*Mal/ FAc
H,H [c]	3500	1250(7.9)			$1.1\cdot10^{4}$	
			410(7.9)		$3.3\cdot10^{3}$	$2.0\cdot10^{4}$
H,Me	4300	920(7.4)			$7.5\cdot10^{4}$(8.9)	$1.7\cdot10^{5}$
			270(7.5)		$1.2\cdot10^{4}$	$1.9\cdot10^{5}$
H,Et(*n*-Alk)	7600	1100(7.5)			$5.4\cdot10^{4}$(7.9)	$2.2\cdot10^{5}$
	33		300(7.5)	34	$1.1\cdot10^{4}$	$2.8\cdot10^{5}$
Me,Me	8500	740 (7.7)			$1.8\cdot10^{5}$	$3.8\cdot10^{5}$
			240(8.0)		$1.1\cdot10^{4}$	$4.0\cdot10^{6}$
Me,OMe	$1.2\cdot10^{4}$	220	1080	50	$1.4\cdot10^{5}$(8.1)	$4.0\cdot10^{5}$(8.6)
	21(8.9)		230(8.1)	82	$3.5\cdot10^{4}$(8.9)	
Me,OAc	$1.2\cdot10^{4}$	1700	4850	58	$8.8\cdot10^{4}$(9.1)	$5.8\cdot10^{5}$(8.7)
	46(7.7)		680(7.4)	79	$1.2\cdot10^{4}$	$3.0\cdot10^{5}$
H,OEt	$1.4\cdot10^{4}$	390(7.7)	320	75	$1.5\cdot10^{5}$(8.3)	$3.0\cdot10^{5}$(8.6)
	14(10.2)		180(8.3)	108	$4.3\cdot10^{4}$	
H,OAc	$1.4\cdot10^{4}$(8.4)	4200(7.2)	7500	18	$6.5\cdot10^{4}$(8.1)	$4.0\cdot10^{5}$(8.8)
	15(5.9)		590(7.7)	41	$1.3\cdot10^{4}$	$2.0\cdot10^{5}$
H,Cl	$2.0\cdot10^{4}$	$1.6\cdot10^{4}$			$7.1\cdot10^{4}$(8.4)	$1.1\cdot10^{5}$
			5000(8.3)		$1.2\cdot10^{4}$	$9.5\cdot10^{4}$
H,$SiMe_3$	$2.3\cdot10^{4}$(8.1)	9600(7.0)	$2.5\cdot10^{4}$	75	$8.9\cdot10^{4}$(8.3)	$2.2\cdot10^{5}$(8.5)
	33(8.4)		2060(7.8)	75	$1.3\cdot10^{4}$(8.4)	$1.0\cdot10^{5}$
Me,Cl	$3.5\cdot10^{4}$	$1.1\cdot10^{4}$	$2.2\cdot10^{4}$	150	$1.6\cdot10^{5}$(8.4)	$9.2\cdot10^{5}$(8.8)
	43		2110(7.9)	120	$1.6\cdot10^{4}$(8.9)	$5.0\cdot10^{5}$
Cl,Cl	$3.2\cdot10^{5}$(8.9)	$3.5\cdot10^{5}$(8.0)	$1.3\cdot10^{6}$	1170(6.9)	$2.7\cdot10^{5}$	$3.9\cdot10^{5}$(8.9)
	460(8.5)		$5.3\cdot10^{4}$(8.1)	603	$3.3\cdot10^{4}$(8.8)	$3.3\cdot10^{5}$
H,CO_2Me	$3.4\cdot10^{5}$	$1.1\cdot10^{6}$	$3.5\cdot10^{7}$	1150(6.6)	$4.9\cdot10^{5}$	$1.1\cdot10^{5}$(8.7)
	430(7.7)		$7.1\cdot10^{5}$(8.7)	370	$1.1\cdot10^{5}$	$1.3\cdot10^{5}$
Me,CO_2Me	$4.9\cdot10^{5}$(8.9)	$6.6\cdot10^{5}$	$1.6\cdot10^{7}$(9.0)	3710	$1.3\cdot10^{6}$	$1.1\cdot10^{6}$(8.9)
	2100(8.1)		$6.0\cdot10^{5}$(8.6)	1590	$2.4\cdot10^{5}$	$1.2\cdot10^{6}$
H,CN	$6.1\cdot10^{5}$	$5.2\cdot10^{6}$	$1.5\cdot10^{8}$	2640(7.2)	$5.4\cdot10^{5}$	$1.5\cdot10^{5}$(8.9)
	2200(8.9)		$1.1\cdot10^{6}$(8.3)	2020	$1.1\cdot10^{5}$(8.4)	$3.5\cdot10^{4}$
H,CHO	$7.4\cdot10^{5}$	$2.8\cdot10^{6}$	$2.7\cdot10^{8}$	1810	$3.8\cdot10^{5}$	$1.1\cdot10^{5}$(8.5)
	2500(8.5)		$2.1\cdot10^{6}$(8.4)	1200	$2.5\cdot10^{4}$(8.5)	$6.4\cdot10^{4}$
Me,CN	$7.9\cdot10^{5}$(8.9)	$1.7\cdot10^{6}$	$4.5\cdot10^{7}$(8.9)	4460	$9.1\cdot10^{5}$	$6.0\cdot10^{5}$(8.7)
	6600(8.4)		$6.7\cdot10^{5}$(8.2)	1060	$1.7\cdot10^{5}$	$1.9\cdot10^{5}$
H,Ph	$2.6\cdot10^{5}$(8.9)	$1.3\cdot10^{5}$(7.6)	$7.3\cdot10^{5}$(7.5)	5500(6.7)	$1.9\cdot10^{6}$	$1.2\cdot10^{6}$(8.8)
	1100(8.6)		$2.3\cdot10^{4}$(8.4)	2410(7.7)	$3.8\cdot10^{5}$	$6.3\cdot10^{6}$
Me,Ph	$3.1\cdot10^{5}$(8.8)	$5.9\cdot10^{4}$	$2.0\cdot10^{5}$(7.5)	6030	$3.9\cdot10^{6}$	$1.3\cdot10^{6}$(8.7)
	850(9.6)		$2.8\cdot10^{4}$(8.6)	2310	$6.6\cdot10^{5}$	$7.7\cdot10^{6}$
Ph,Ph	$7.8\cdot10^{5}$(7.9)	$1.0\cdot10^{6}$	$7.1\cdot10^{5}$(6.9)	$1.0\cdot10^{4}$(7.0)	$1\cdot10^{7}$	$2.4\cdot10^{6}$(8.6)
	4100(8.5)		$1.4\cdot10^{5}$(8.3)	7010	$2.4\cdot10^{6}$	$6.9\cdot10^{6}$

Before discussing the data, we compare them with high pressure gas-phase results because the theoretical calculations refer to isolated molecules. There are no recent directly determined absolute gas-phase addition constants. However, the available older data make clear that the reactions are considerably faster in solution by factors ranging from about 5 to 80. On average, the frequency factors are practically identical, and the differences are due to an average 6.5 ± 2.3 kJ/mol lower activation energy for the liquid-phase reactions. Solvation effects certainly play a role, but one finds only very minor solvent effects on the solution rate constants. Even for the highly nucleophilic *t*Bu radical adding to the very electron-deficient acrylonitrile, the rate constant increases only by a factor of 3 upon changing the solvent from alkanes to acetonitrile. Alternatively, the difference may come from the internal pressure of the solvent. In fact, one obtains the correct rate constant ratio by using an activation volume of about -15 cm^3/mol which is known from polymerization data.[3]

Theoretical Results

The structures and the charge distribution of the TS, the reaction barriers and the reaction enthalpies H_r were calculated for the addition of Me, MOH, MCN and *t*Bu to various alkenes. For very reliable methods phenyl-substituted compounds are still out of reach. Many quantum chemical techniques at different theoretical levels were applied, ranging from computationally efficient to computationally demanding ones. A good agreement of the theoretical barriers with experimental solution activation energies back-corrected to 0°K is reached within the experimental error bars only by very high level ab initio methods such as CBS-RAD and G3(MP2)-RAD. These involve large basis sets and extensive electron correlation. B3-LYP/6-31G(d) works reasonably well but some popular methods like AM1, UHF and UMP2 prove to be very unreliable and do not even reproduce the trends of the experimental data. The main lesson is that all authors using available programs for the calculation of energy barriers for radical additions must first critically assess the method against now established cases. The reaction enthalpies are slightly less sensitive to the choice of method but must also be critically assessed. On the other hand, the calculation of reliable transition state geometries needs less effort.

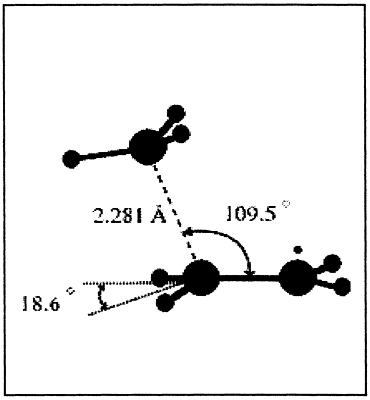

Figure 1. TS structure for Me + ethene.

Figure 1 shows the transition state for the addition of methyl to ethene, and very similar structures hold for the other additions. The newly formed bond is still long, but the angle of attack is already close to the final bond angle. The methyl radical and the attacked CH_2-group exhibit considerable out-of-plane deformations. Moreover, the hydrogen atoms of Me and of the CH_2-group are staggered.

The calculations also reveal that the TS length of the new bond increases with increasing exothermicity of the additions, as is expected from Hammond's postulate. Further, the TS charge distributions characterize Me as an electron acceptor for most alkenes and as a donor only for the strongly electron-deficient alkenes acrylonitrile and acrolein. Hence, in contrast to earlier belief, Me is not generally nucleophilic, and its barriers decrease linearly with increasing calculated reaction enthalpies. On the other hand, MOH acts generally as a donor and MCN as an acceptor, and this points to the stronger polar effects in their reactions.

Frequency Factors

All additions to monosubstituted and 1,1-disubstituted alkenes occur dominantly at the unsubstituted alkene carbon atom. This makes specific steric effects of the more remote alkene substituents unlikely, and Table 1 discloses none. For each radical the frequency factors vary with alkene substitution, in some cases up to two orders of magnitude. However, there is no systematic trend, and for the individual radicals the numbers cluster around an average with rather small standard deviations. Therefore, we believe that the variations of frequency factors with alkene substitution are not significant but are due to the known error compensation of Arrhenius parameters.[4] In fact, exceptionally low/high frequency factors always go parallel with exceptionally low/high experimental activation energies.

The frequency factors should decrease with increasing loss of motional entropy upon approach to the TS. Therefore, one expects larger frequency factors for primary than for secondary radicals, and larger values for secondary than for tertiary radicals. For the latter, Figure 1 suggests the strongest motional hindrance in the TS. This view is strongly supported by the average experimental frequency factors. They are relatively large for the primary species, $\log(A/\mathrm{M}^{-1}\mathrm{s}^{-1}) = 8.6 \pm 0.4$ for Me, 8.6 ± 0.6 for Bn, 8.1 ± 0.1 for MOH, 8.4 ± 0.3 for MEst and 8.7 ± 0.3 for MCN, smaller for the secondary open-chain malonyl and the 1-*tert*-butoxycarbonyl ethyl radical, 8.2 ± 0.3 and 7.9 ± 0.5[5], and smallest for the tertiary species, $\log(A/\mathrm{M}^{-1}\mathrm{s}^{-1}) = 7.3 \pm 0.4$ for *t*Bu, 6.9 ± 0.3 for PEst and 7.7 for PCN. Hence, we suggest general ranges for frequency factors of additions of small radicals to alkene CH_2-groups as $\log(A/\mathrm{M}^{-1}\mathrm{s}^{-1}) = 8.5 \pm 0.5$ for methyl and all primary radicals, $\log(A/\mathrm{M}^{-1}\mathrm{s}^{-1}) = 8.0 \pm 0.5$ for secondary radicals, and $\log(A/M^{-1}s^{-1}) = 7.5 \pm 0.5$ for tertiary radicals. These values were used to obtain the somewhat smoothed activation energies used in the further discussion from the rate constants, and they are probably more reliable than the original data from the Arrhenius plots.

In accord with the entropy considerations, cMal has a higher average $\log(A/M^{-1}s^{-1}) = 8.7 \pm 0.2$ because its rigid structure does not allow large entropy losses in the TS. Alkynes lack the degree of freedom of rotation about the CC-bond, and consequently the addition frequency factors are about one order of magnitude larger than those for alkenes. A similar reasoning applies to the decrease in A upon substitution at the attacked site.[2] Finally, unusually large frequency factors are found for the very fast additions of POH to very electron-deficient alkenes. This and the small activation energies of about 10 kJ/mol indicates the onset of diffusion-controlled kinetics and, hence, in these cases the true activation energies must be close to zero. In total, the frequency factors are well explained by considerations of the activation entropy but extensive calculations with high level theories are still scarce.

The State Correlation Diagram

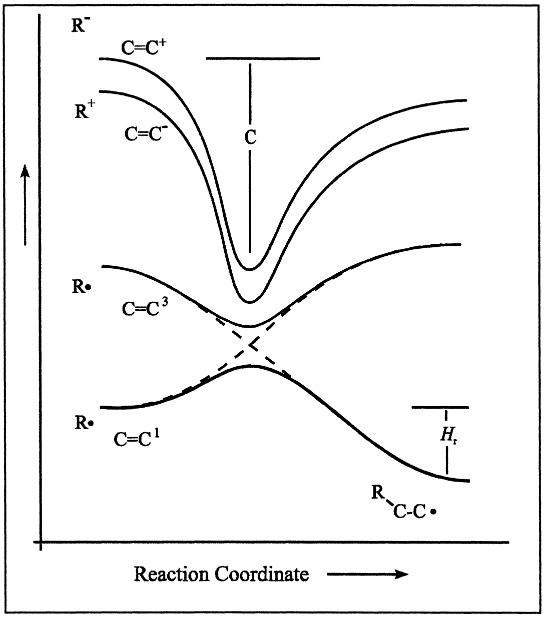

Figure 2. State correlation diagram for a radical addition.

In the last two decades Shaik, Pross and coworkers[6] have developed a pictorial method for the rationalization of the barriers for many types of chemical reactions. It rests on the evolution of electronic configurations along the reaction coordinate, is strongly supported by valence-bond (VB) calculations and goes essentially back to London's explanation of the barrier of the H + H_2 exchange reaction. For a radical addition (Figure 2) one considers primarily the two energetically lowest VB configurations, namely the ground configuration with the alkene in the singlet state and the first excited configuration where the alkene is a $\pi\pi^*$ triplet. If these configurations were retained upon approach of the reactants, the ground configuration would correlate with an excited configuration of the product whereas the ground configuration of the product would resemble the excited educt. However, the configurations interact, and their avoided level crossing leads to the barrier at the TS. It is clearly seen from Figure 2 that the barrier should decrease with increasing exothermicity of the reaction. It also should decrease with decreasing alkene triplet energy, and any decrease should lead to an earlier TS, that is, a longer forming bond.

Polar effects enter quite naturally through the admixture of CT configurations. For the reactant geometry these have high energies of approximately *IE*(radical) – *EA*(alkene) and *IE*(alkene) – *EA*(radical), respectively. In the TS these energies are considerably reduced by the Coulomb attraction *C* of the ions, and they may approach the energies of the lower configurations and mix with them. Of course, this admixture will depend on an interaction strength parameter which is related to the overlap of the pertinent molecular orbitals and may differ from system to system.

Qualitatively one thus expects reductions of the barriers and consequently larger rate constants by nucleophilic polar effects if *IE*(radical) – *EA*(alkene) is small and by electrophilic polar effects if *IE*(alkene) – *EA*(radical) is small. An ambiphilic reaction pattern is expected if both energy differences are small, and then a given radical exerts nucleophilic effects towards electron-deficient alkenes and electrophilic effects towards electron-rich alkenes. The Coulomb attraction is diminished by charge delocalization over radical and alkene substituents. Hence, additions involving phenyl-substituted radicals like benzyl, styryl and cumyl, and phenyl-substituted alkenes like styrene should be less subject to polar effects than their less conjugated hydrocarbon counterparts.

The state correlation diagram of Figure 2 also shows that polar effects can only diminish the reaction barriers. Normally, the latter will not fall below zero, but for very strong CT interactions the CT configurations may even cause intermediate minima on the reaction coordinate. Finally, the diagram indicates that the enthalpic and the polar effects on the barriers can not be simply additive or composed of factors which characterize the radicals and the alkenes individually such as *Q*, *e* or other constants.

Activation Energies

In searches for correlations between the activation energies and the enthalpic and polar factors, linear regressions of E_a with H_r, *EA*(alkene) and *IE*(alkene) were performed. The reaction enthalpies were mostly estimated from R-H and RA-H bond dissociation energies and heats of formation of RH, A and RAH via the thermodynamic cycle

$$RH + A \longrightarrow R\bullet + H\bullet + A \longrightarrow R\text{-}A\bullet + H\bullet \longrightarrow RA\text{-}H \longrightarrow RH + A$$

and generally have errors of at most 10 kJ/mol. Data for *EA* and *IE* are available from the literature. The results of these correlations were confusing. Thus, all nucleophilic or weakly nucleophilic radicals, all ambiphilic radicals and even all the weakly electrophilic radicals gave good correlations of E_a both with H_r and with the alkene *EA* although with different slopes and intercepts. On the other hand, the strongly electrophilic radicals did not give satisfactory correlations neither with H_r nor with the alkene *IE*.

A closer inspection of the data reveals that the parameters H_r, *EA*(alkene), *IE*(alkene) and the alkene triplet energies are themselves strongly correlated. Thus, the triplet energy decreases linearly with increasing exothermicity, and, therefore, a specific influence of the triplet energy is not detected. Further, substituents which make alkenes more electron-deficient (CN, CHO) generally make the reaction more exothermic because they also stabilize the adduct radical more than the alkene. Hence, favorable enthalpic and nucleophilic polar effects

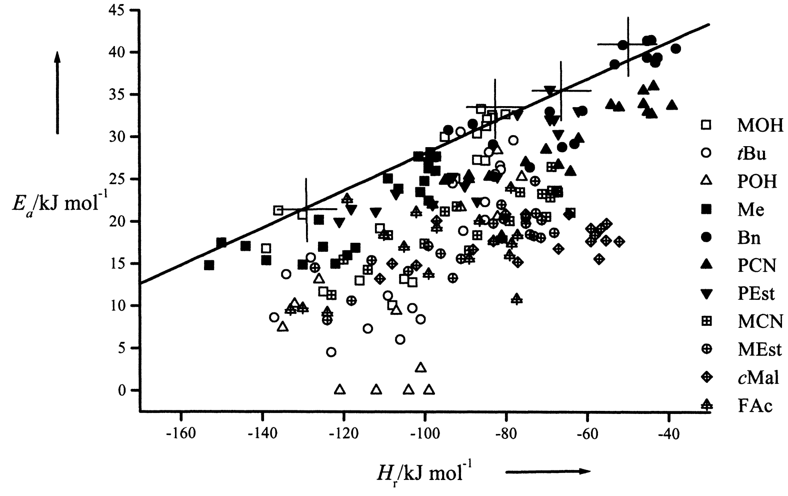

Figure 3. Activation energies of all additions of Table 1 vs. the reaction enthalpies. The crosses indicate the experimental errors.

reinforce each other in individual plots, and, hence, in correlations with the alkene *EA* even radicals without or with only small polar effects appear to be nucleophilic. In contrast, substituents which make alkenes more electron rich (alkyl, O-alkyl) render the addition less exothermic, that is, favorable enthalpic and electrophilic effects cancel each other in plots of E_a vs. H_r and *IE*. These parameter interrelations make linear regressions nearly meaningless and sometimes deceiving. They have even led to wrong conclusions in the literature. The use of polar Hammett constants does not help because they also correlate well with the ionization energies and electron affinities.

The state correlation diagram now suggests that the enthalpy effect should provide an upper limit for the activation energies, and a plot of all data vs. H_r should reveal this limit. Figure 3 shows that this limit does exist. It is a straight line as suggested by Evans-Polanyi-Semenov and is given by $E_a = 50 + 0.22\ H_r$. Because of polar effects most of the experimental activation energies are below the line.

Since E_a will not be negative, the polar effects will reduce E_a by factors ranging between 0 and 1. This leads to the general predictive equation

$$E_a = (50 + 0.22H_r)F_nF_e. \qquad (1)$$

The nucleophilic factor F_n should decrease from 1 to 0 with decreasing energy gap *IE*(radical) – *EA*(alkene) and increasing Coulomb term C_n and/or orbital interaction parameter γ_n. The electrophilic factor F_e depends in the same way on *IE*(alkene) – *EA*(radical), C_e and γ_e. The energies *IE* and *E*A are known, and *C* should not be larger than the 6.6 eV calculated for two point charges at the reaction distance of Figure 1. Moreover, *C* and γ should be small for phenyl-substituted radicals and alkenes, and F_n and F_e should approach zero when *C* matches the energy gaps. Otherwise, not much can *a priori* be said about the functional dependence of *F*, and the parameters may even vary from system to system. We suggest the function

$$F = 1 - \exp(- [(IE - EA - C)/\gamma]^2) \qquad (2)$$

which has the correct limiting properties.

Fortunately, the parameters *C* and γ fall into narrow ranges for specific radicals and alkenes. Figure 4 demonstrates that the additions of the three strongly nucleophilic radicals MOH, *t*Bu and POH to all alkenes except the phenyl-substituted ones (open symbols) are accommodated by one common nucleophilic function (C_n = 6.2 eV, γ_n = 1.7 eV, line b). For methyl both C_n

and γ_n are larger (6.5 eV, 3.2 eV, line a), which is probably due to the more localized charge and spin. As expected, the additions of all four radicals to phenyl-substituted alkenes require a smaller $C_n = 5.7$ eV and a smaller $\gamma_n = 1.0$ eV (line c). As can be seen from Figure 4, Me is not very nucleophilic in spite of the larger parameters because the energy gaps are large. Electrophilic effects of these radicals are not detectable.

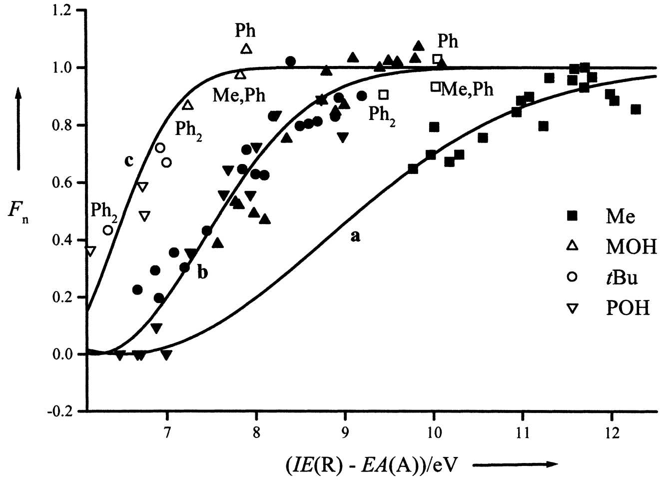

Figure 4. Nucleophilic polar factors.

A comprehensive analysis for all the additions of Table 1 shows a rather good agreement between the experimental and calculated activation energies, with a standard deviation of 2.4 kJ/mol for the following polar factors (in eV, phenyl-substituted alkenes in brackets): Me $C_n = 6.5(6.0)$, $\gamma_n = 3.2(2.0)$, Bn $C_n = 5.5(5.0)$, $\gamma_n = 1.5(0.75)$, MOH, *t*Bu and POH $C_n = 6.0(5.5)$, $\gamma_n = 2.0(1.0)$, PCN $C_n = 6.0(5.5)$, $\gamma_n = 2.0(1.0)$, $C_e = 4.5(4.2)$, $\gamma_e = 2.5(2.5)$, PEst $C_n = 6.0(5.5)$, $\gamma_n = 1.5(0.75)$, $C_e = 4.5(4.0)$, $\gamma_e = 2.0(2.0)$, MCN $C_n = 6.0(5.5)$, $\gamma_n = 3.0(2.0)$, $C_e = 4.5(4.2)$, $\gamma_e = 3.0(3.0)$, MEst $C_n = 6.0(5.5)$, $\gamma_n = 3.0(1.5)$, $C_e = 4.5(4.0)$, $\gamma_e = 3.0(3.0)$, cMal $C_e = 4.0(3.5)$, $\gamma_e = 4.3(3.5)$, FAc $C_e = 4.5(4.0)$, $\gamma_e = 3.0(2.5)$. Radicals are ambiphilic when both nucleophilic and electrophilic factors are required. The nucleophilic parameters C and γ are always larger than their electrophilic counterparts.

The polar parameters can be interpolated and extrapolated to other radicals such as n-alkyl, cumyl, substituted benzyl and perfluoroalkyl species, and combination of the calculated activation energies with the predicted frequency factors reproduces their experimental addition constants to many alkenes over seven orders of magnitude within deviations below factors of ten.[2] Despite this success, our predictive equation and the magnitudes of the parameters C and γ still need more rigorous theoretical foundations, of course.

Relations to Polymer Chemistry

Homopropagation. Table 1 lists recent homopropagation coefficients for several monomers at room temperature and their Arrhenius parameters, together with the corresponding rate data for the addition of electronically similar low molecular weight radicals to the same monomers. EEst is 1-*tert*-butoxycarbonylethyl. To obtain the activation energies for the small radicals from the rate constants the recommended average frequency factors were used. The addition of most small radicals is considerably faster than the propagation but similar factors operate in the two processes because the gross ordering of the data is the same. The propagation coefficient of methylacrylate appears exceptional and may reflect difficulties in measurements of very large values. A closer inspection of Table 1 shows that there is not much difference between the activation energies of the low and the high molecular weight species with the exception of ethene for which the addition of Me is probably not the optimum model system. On the other hand, the frequency factors of propagation are all significantly smaller than the frequency factors of the small radical additions. This means a larger entropy loss of polymeric radicals on approach to the TS. Moreover, as for the small radicals, the frequency factor of k_p is smaller for the tertiary polymeric radicals (MAN, MMA) than for the primary or secondary species (ethene, styrene, MA). Hence, with the reduced frequency factors the equations of the last section may well serve to predict propagation rate constants within about an order of magnitude.

Table 2. Comparison of propagation rates with addition rates of similar small radicals at or close to 300°K.

monomer/model reaction	k_p/k /$M^{-1}s^{-1}$	$\log(A/M^{-1}s^{-1})$	E_a/kJ mol^{-1}
ethene/ Me + ethene	20/7000	7.3/8.5	34.3/28.2
styrene/ Bn + styrene	93/1100	7.6/8.5	32.5/30.8
methylacrylate/EEst + MA	19000/15000	7.2/7.9	17.7/21.1
methacrylonitrile/PCN + MAN	18/1060	6.4/7.5	29.7/26.4
methylmethacrylate/PEst + MMA	345/3710	6.4/7.5	22.4/22.4

Copolymerization. The view of very similar controlling factors in propagation and small molecule additions is strongly supported by a good correlation between reactivity ratios r_1 of several monomers M with the ratios of rate constants for the addition of small model radicals to M and M' $r_{1,calc} = k(M)/k(M')$. An example is given in Figure 5 (line slope 0.92, $R^2 = 0.90$) and similar plots are found for the pairs EEst/MA, MEst/MA, PEst/MMA, MCN/AN and PCN/MAN.

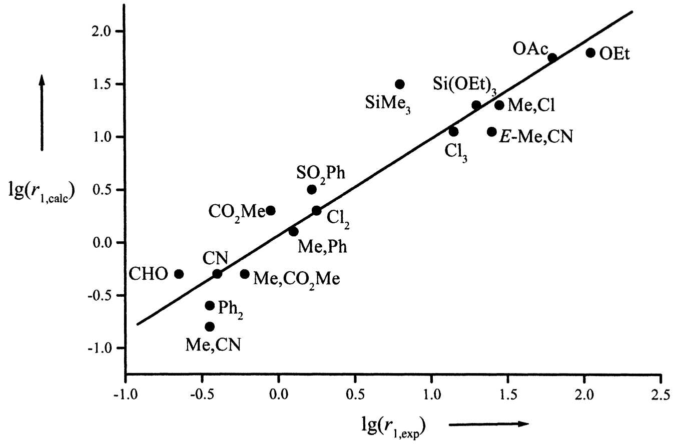

Figure 5. Experimental and estimated reactivity ratios r_1 for styrene.

A Penultimate Effect. Recently, the rate constants for the addition of monomeric radicals of methylacrylate and of methyl methacrylate with different β-substituents (penultimate groups) to their monomers were measured with a new ESR method.[7] Table 3 shows that the rate constants are significantly smaller for the tertiary substituents *t*Bu and POH than for the smaller groups MOH and Ph.

Table 3. Rate constants for the addition of monomeric and polymeric radicals of MA and MMA to their monomers.

reaction	$k_{300}/M^{-1}s^{-1}$	reaction	$k_{300}/M^{-1}s^{-1}$
Ph–MA• + MA	22'400	Ph–MMA• + MMA	2'640
MOH–MA• + MA	18'110	MOH–MMA• + MMA	3'290
*t*Bu–MA• + MA	6'120	*t*Bu–MMA• + MMA	600
POH–MA• + MA	3'290	POH–MMA• + MMA	1'205
MA-homopropagation	19'000	MMA-homopropagation	345

All monomeric radicals add faster to MMA than the polymeric species, and this agrees with the assumption of a general decrease with increasing chain length. However, for MA the addition constants of the monomeric radicals with tertiary β-substituents are smaller than the propagation constant which refers to a secondary penultimate group. Overall, the β-substituent effects are not huge, and their order of magnitude agrees with the selectivity ratios of the penultimate effect found in copolymerizations.

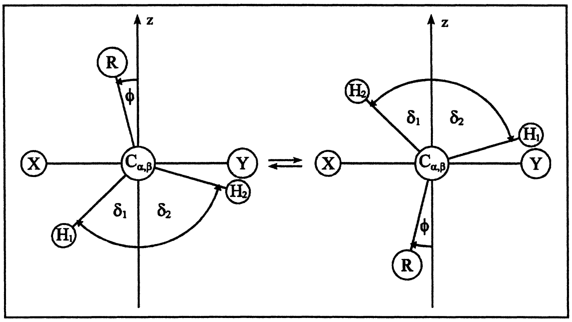

Figure 6. Equilibrium conformations of propagating radicals.

Actually, a qualitative interpretation is easily found by a consideration of the radical and the TS structures. From ESR spectroscopy it has long been known[8] that radicals of the type R-CH_2-CXY• with one α-carboxy group have planar radical centers.

They exchange between the two energetically equivalent average conformations shown in Figure 6. The adducts to MMA exhibit rather high conformational barriers. This causes line-broadening effects which have in early times and even recently led to misinterpretations of the 5 + 4 line ESR spectrum of the MMA propagation radical. The adducts to MA have smaller barriers. Further, the average angle ϕ is small for MMA and large for MA adducts, and it decreases with increasing bulkiness of the β-substituent R. Hence, monomeric, dimeric and longer-chain radicals are distinguished in ESR-spectra via the different β-hydrogen coupling constants.[8]

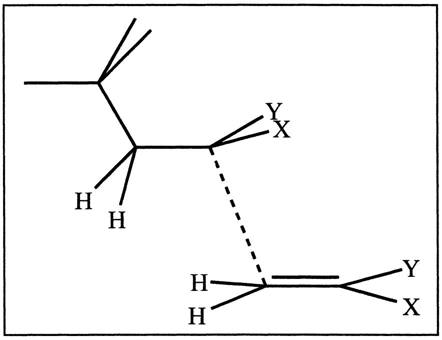

Figure 7. TS for the addition of monomeric radicals.

Figure 7 shows the structure of the TS expected from Figure 1. In comparison to the equilibrium structures (Figure 6), the adding radicals have to undergo geometrical changes to reach the TS. Firstly, the β-substituent has to be aligned with the newly-formed C-C-C-C-plane. This will be more costly in energy and entropy terms for more bulky β-residues.

A difference between acrylates and methacrylates is expected but the ratios of rate constants in Table 3 are not very different for the two monomers so that the coplanarity requirement seems not to be important for the change of the rate constants. Secondly, the α-substituents X and Y have to be bent towards the β-substituent R. This is certainly energetically more costly for tertiary groups R, and this leads to higher activation energies. Moreover, the rotation of the tertiary groups R about the C_β-C_γ-bond will be more hindered than that of less bulky substituents. This decreases the frequency factor of addition. Hence, radicals carrying penultimate units with tertiary substituted γ-carbon atoms should always show lower rate constants than those with less substituted carbons. This agrees with the observation that the rate constants for tertiary substituted MA-monomer radicals are smaller than the propagation constant. Further proof of this hypothesis is clearly required.

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