# Rate Constants for Some Prototype Radical Reactions in Liquids by Kinetic Electron Spin Resonance

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During the past decade free-radical reactions have gained new interest in organic synthesis since they suffer less from substituent incompatibilities than their ionic counterparts.[1,2] Most of the high-yielding schemes use radical chain reactions in which the chain-carrying steps are so fast that other possible reactions cannot interfere. In the past, such processes were usually discovered by accident, and failures in generalizations occurred. Today, their design and applications can greatly profit from the advanced knowledge of radical reaction rate constants. Consider the chain addition of aldehydes to substituted alkenes:

$$R-\dot{C}O + CH_2=CHX \rightarrow R-CO-CH_2-\dot{C}HX$$

$$R-CO-CH_2-\dot{C}HX + R-CHO \rightarrow$$
$$R-CO-CH_2-CH_2X + R-\dot{C}O$$
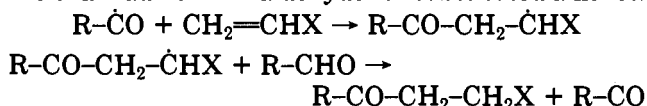
It fails completely with certain aldehydes and substituents but works well with others.[1,3,4] We know now that this is so, because the rate constants of the chain steps and of the major interfering reactions, namely, decarbonylation of R–ĊO and telomerization, vary by orders of magnitude with substitution of aldehyde and alkene, and for success proper combinations must be chosen.

Recently, compilations of individual rate constants have been prepared which can serve as bases for such selections.[5–8] Yet, their general use is still limited: Firstly, many data were obtained in indirect ways and may be subject to fairly large errors. Secondly, for many reactions one finds only special examples and data for one temperature, and extrapolations are hindered by the order of magnitude variations. Therefore, comprehensive discussions and developments of predictive structure–reactivity relations for classes of radical reactions have remained scarce.

This Account summarizes our efforts to obtain rationalizations of rate constants for several important typical radical reactions. We first briefly describe experimental techniques which provided large series of rate constants in direct ways for liquid-phase reactions. Then we analyze data for (1) radical self-reactions (2R• → products), (2) addition reactions of nucleophilic alkyl radicals to alkenes, and (3) the decarbonylation of acyl radicals (R–ĊO → R• + CO).

## Kinetic Electron Spin Resonance

Direct determinations of radical rate constants require time-dependent generations, observation of the

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response of the radical concentrations, and analysis of this response in terms of rate laws.
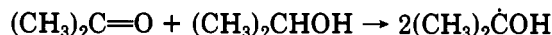
For the radical generation we use photochemical systems which produce the desired radicals in clean ways; i.e., product distribution studies ensured the absence of disturbing side reactions. In particular, the type I cleavage of symmetric ketones followed by the activated decarbonylation

$$R-CO-R \rightarrow R-\dot{C}O + R^\bullet$$

$$R-\dot{C}O \rightarrow R^\bullet + CO$$
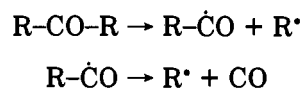
yields alkyl and acyl radicals (R = CH$_2$OH, (CH$_3$)$_2$COH, (CH$_3$)$_2$CH, (CH$_3$)$_3$C, benzyl). The peroxide method[9] works cleanly with fast hydrogen donors

$$(CH_3)_3COOC(CH_3)_3 \rightarrow 2(CH_3)_3CO^\bullet$$

$$(CH_3)_3CO^\bullet + RH \rightarrow (CH_3)_3COH + R^\bullet$$
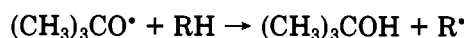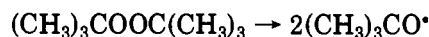
(R = CH$_2$OH, (CH$_3$)$_2$COH) as do certain photoreductions, e.g.

$$(CH_3)_2C=O + (CH_3)_2CHOH \rightarrow 2(CH_3)_2\dot{C}OH$$

The fragmentation of aliphatic esters to alkyl and alkyloxyacyl species has also been applied. Photolysis of the substrate solutions occurs within the probehead of conventional electron spin resonance (ESR) spectrometers. They detect the radicals and measure their concentrations. ESR is particularly suited for kinetic studies since calibration problems are more easily solved as with other methods,[10] and its versatility and utility have elegantly been reviewed in these accounts.[9] There, Griller and Ingold also described the basic time-resolved experiment: The UV light of a strong (1 kW, Hg/Xe) lamp is focused intermediately upon a slit and chopped

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(2) *Substituent Effects in Radical Chemistry*; Viehe, H. G., et al., Eds.; Reidel: Dordrecht, 1986.

(3) Karasch, M. S.; Urry, W. H.; Kuderna, B. M. *J. Org. Chem.* 1949, 14, 248.

(4) Abell, P. I. In *Free Radicals*; Kochi, J. K., Ed.; Wiley: New York, 1973 and references therein.

(5) *Handbook of Biomolecular and Termolecular Gas Reaction*; Kerr, J. A., Moss, S. J., Eds.; CRC: Boca Raton, FL, 1981; Vol. I, II.

(6) Ross, A. B.; Neta, P. *Rate Constants for Reactions of Aliphatic Radicals in Aqueous Solution*; National Bureau of Standards; Washington, DC, 1982; NSRDS-NBS 70. See also: NSRDS-NBS 43, 51, 59, 65.

(7) *Radical Reaction Rates in Liquids*; Fischer, H., Ed.; Springer-Verlag: West Berlin, 1983–1985; Landolt-Börnstein, New Ser., Vols. II/13a–e.

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(10) Paul, H. In *Chemical Kinetics of Small Organic Radicals*; Alfassi, Z., Ed.; CRC: Boca Raton, FL, in press.

there with a fast rotating sector (period typically 5–50 ms, on/off ratio 1:4). Many response traces of radical signals (here 50 000–300 000) are accumulated coherently in a digital storage until a good signal-to-noise ratio is obtained. The signal intensity is converted to concentration units by calibration against signals of stable radical samples (e.g., galvinoxyl) of known concentrations. Finally, the kinetic traces are analyzed by fitting rate equations to them. As an alternative to this time-resolving technique, we also use a modulation method.[10] In this method, the slit is replaced by a sine-shaped diaphragm, and the optics is such that the light flux at the sample varies harmonically with time. Then the radical concentration also oscillates but with a certain phase shift reflecting the kinetics. This is determined by phase-sensitive detection at the modulation, i.e., sector, frequency and analyzed.

Before presenting examples, we wish to point out (more to the specialist than to the hasty reader) a number of technical measures which were introduced to increase the reliability of the kinetic results: (a) flowing samples[11] to avoid depletion of substrates or side reactions with products and to keep the conversions below about 5%; (b) thermostated flat cells and optimized optics to ensure a homogeneous light flux over the sample surface;[11,12] (c) the use of low substrate concentrations to avoid inhomogeneities along the sample depth[13] (optical densities lower than 1 are tolerable); (d) stabilization of the lamp output to avoid fluctuations during the time of measurement;[12] (e) the use of fairly low maximum radical concentrations ($\leq 5 \times 10^{-7}$ M), i.e., generation rates, to avoid effects of chemically induced electron polarization which hinder concentration determinations;[12] (f) reduction of the spectrometer response time of commercial instruments from ca. 300 to 20 μs and the installation of microwave amplifiers to regain sensitivity;[14,15] (g) square-wave field modulation techniques to correct for eventual base line drifts or offsets by subtraction procedures;[16,17] (h) the use of substandards and saturation-free double integrals in the calibrations;[12] (i) the refinement of the analysis procedures by gradually shifting from "forced fitting" to rigorous methods which involve extensive stability and significance tests.[16–20]

In the following we only present data of recent work which have statistical errors well below 20%. The total errors are certainly larger due to systematic uncertainties but probably not much since for several cases redeterminations by different co-workers using independent techniques gave results which were identical within statistical errors.

The first example demonstrates time-resolved ESR and our most advanced analysis procedure: During photolysis of *tert*-butyl pivalate one observes *tert*-butyl
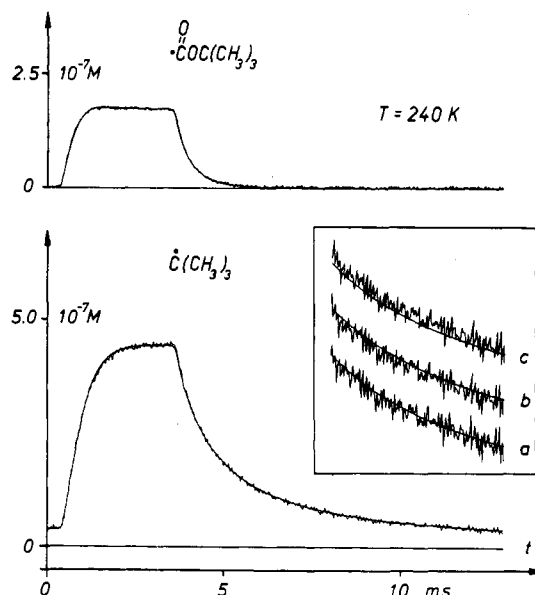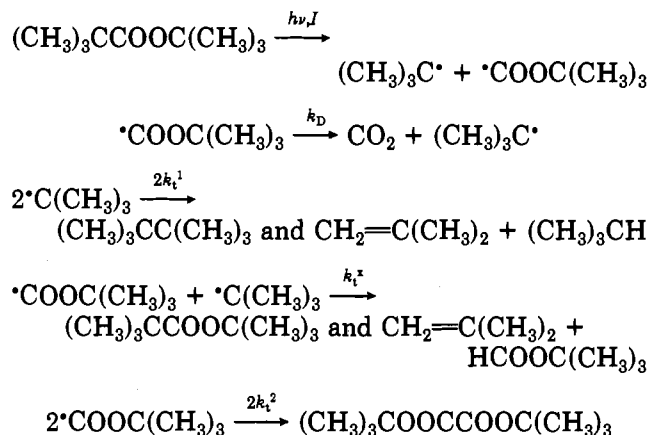

Figure 1. Concentration vs. time profiles for *tert*-butyl and *tert*-butoxyacyl radicals during intermittent photolysis of *tert*-butyl pivalate in *n*-heptane. Noiseless trace and insert (a): best fit, $\chi^2 = 1.049$. Insert (b): $k_1 = 500$ s^{-1} fix, six free parameters, $\chi^2 = 1.16$, i.e., 106 standard deviations above minimum. Insert (c): $2k_t^1 = k_t^x = 2k_t^2$ fix, five free parameters, $\chi^2 = 1.31$, i.e., 273 standard deviations above minimum.

and *tert*-butoxyacyl radicals.[20,21] Within 97% the product distribution is accounted for by the reactions

$$(CH_3)_3CCOOC(CH_3)_3 \xrightarrow{h\nu,I}$$
$$(CH_3)_3C^\bullet + {}^\bullet COOC(CH_3)_3$$

$${}^\bullet COOC(CH_3)_3 \xrightarrow{k_D} CO_2 + (CH_3)_3C^\bullet$$

$$2{}^\bullet C(CH_3)_3 \xrightarrow{2k_t^1}$$
$$(CH_3)_3CC(CH_3)_3 \text{ and } CH_2{=}C(CH_3)_2 + (CH_3)_3CH$$

$${}^\bullet COOC(CH_3)_3 + {}^\bullet C(CH_3)_3 \xrightarrow{k_t^x}$$
$$(CH_3)_3CCOOC(CH_3)_3 \text{ and } CH_2{=}C(CH_3)_2 + HCOOC(CH_3)_3$$

$$2{}^\bullet COOC(CH_3)_3 \xrightarrow{2k_t^2} (CH_3)_3COOCCOOC(CH_3)_3$$

This scheme contains five unknown rate parameters which we wish to determine. The noisy traces of Figure 1 show the time dependence of the concentrations of the two radicals (150 000 averages and 512 data points for each). The rate equations for the system are of mixed first and second order and cannot be solved analytically. Therefore, a numeric integration (Runge–Kutta–Fehlberg, seventh order) was coupled to a least-squares (χ^2) minimization (Simplex) and employed to directly fit them to the two data sets. In this procedure the time variation of the generation and the closure condition for the concentrations at the start and end points of the time window are taken into account.[20] Furthermore, the ratio of the radical concentrations was treated as a free parameter since it could be measured to only ±20% accuracy.[20] Finally, for testing purposes an additional first-order decay (k_1) of the acyl radical was introduced for which there is no basis from the products. Independent of the starting parameters, fits

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(21) Kaiser, T.; Grossi, L.; Fischer, H. *Helv. Chim. Acta* **1978**, *61*, 223.
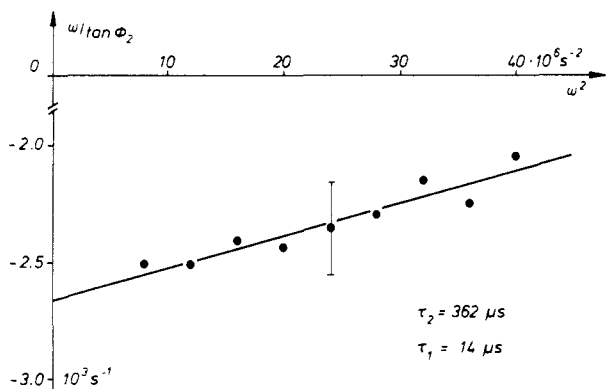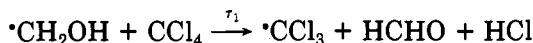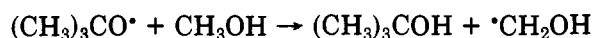
Figure 2. Phase angle effects on the delayed generation of trichloromethyl radicals by $\cdot CH_2OH + CCl_4$.

converged to the result shown as noiseless traces overlaying the noisy ones in Figure 1 ($I = 4.5 \times 10^{-3}$ M s^{-1}, $k_D = 1300$ s^{-1}, $2k_t^1 = 2.6 \times 10^9$ M^{-1} s^{-1}, $k_t^x = 2.2 \times 10^9$ M^{-1} s^{-1}, $2k_t^2 = 1.0 \times 10^9$ M^{-1} s^{-1}, concentration ratio 0.39, $k_1 = 4 \times 10^{-2}$ s^{-1}) at a satisfying $\chi^2 = 1.049$ per degree of freedom. k_1 is found close to zero; i.e., the improbable reaction is in fact insignificant. To many readers who are not familiar with multiparameter fitting the determination of seven kinetic parameters from two traces may seem fairly demanding. However, we do have 1024 data points at our disposal, and not just a few. Moreover, as the insert of Figure 1 demonstrates, fixing of some of the unknowns even within reasonable limits as (b) $k_1 = 500$ s^{-1} < $k_D = 1300$ s^{-1} or (c) equal termination constants leads to visibly worse agreements.

The second example refers to modulation spectroscopy and displays a particular feature of this versatile technique.[22,23] During photolysis of di-*tert*-butyl peroxide in methanol containing CCl_4, one observes the radical $\cdot CCl_3$, which is produced only by the fast reactions

$$(CH_3)_3CO\cdot + CH_3OH \rightarrow (CH_3)_3COH + \cdot CH_2OH$$

$$\cdot CH_2OH + CCl_4 \xrightarrow{\tau_1} \cdot CCl_3 + HCHO + HCl$$

and then decays more slowly by self-termination. Figure 2 shows the phase shift angle of the observed radical plotted in a special way against the square of the modulation frequency. For the analysis of such data analytical solutions have been developed[22-27] which rest on linearizations of the differential rate equations for high modulation frequencies. For the present case the plot of Figure 2 should give a straight line determined by the lifetime τ_2 of the observed radical and by the lifetime of the precursor radical τ_1, i.e., the rate of the electron transfer from $\cdot CH_2OH$ to CCl_4. From the intercept and slope the two time constants are easily derived (see Figure 2). One notes that even in a case where one radical transforms so rapidly into another that it cannot be observed directly, its decay rate is still determinable from the small induction phase shift transferred to the oscillation of the secondary species.

While these examples refer to advanced analysis procedures for complex reaction systems, simpler procedures for less involved systems[12,15,24] are also available and have been used to obtain most of the data for the following sections.

The Self-Reaction

The bimolecular reaction between two carbon-centered radicals occurs in liquids with very high rate constants (10^8–10^{10} M^{-1} s^{-1}) unless the approach of the radical centers is specifically hindered by bulky substituents. Usually the rate constants decrease with increasing viscosity, and this is considered as evidence for a rate determination by diffusive encounters. Solving Fick's law for spherical species which react on every encounter, von Smoluchowski[28] derived (1917) an equation from which diffusion-controlled rate constants can be predicted from diffusion coefficients (D) and reaction distances (ρ). If one allows for finite rates for the reaction on encounter ($2k_\infty$) and for the spin statistics, the equation reads for radicals[29]

$$2k_t/M^{-1} \, s^{-1} = 2k_t^s/(1 + 2k_t^s/2k_\infty)$$

with

$$2k_t^s = \sigma 8\pi 1000^{-1} N_L D\rho$$

The spin statistical factor is $\sigma = 1/4$ if there are no triplet–singlet transitions during the encounter. Refinements of the general theory to allow for chemical anisotropy of the particles and its averaging by reorientational and translation motions, for effects of hydrodynamic repulsion and the attractive potential experienced on collision, and for the more jumplike diffusion of small species are numerous and theoretically challenging.[29,30] In part, they predict gross deviations from predictions obtained from the classical formula. Unfortunately, the comparison with experimental data is hampered by the fact that σ, ρ, and D are not known exactly. Therefore, it has been customary to estimate D via the Stokes–Einstein relation and to assume that $2k_\infty \gg 2k_t^s$ and that $\sigma = 1/4$. This simplifies the original equation to $2k_t = RT/1500\eta$, so that only temperature and viscosity (η) are needed to estimate $2k_t$. For many years it has been known,[32] however, that the Stokes–Einstein relation does not hold for solutes which are of similar size as the solvent molecules, i.e., also for small radicals in usual solvents. Consequently, any gross agreement of data with the simplified equation cannot be considered a rigorous test of diffusion control, nor can it be used to check more recent theoretical predictions.

In the past years we have found a somewhat more realistic approach to the problem of estimating D, σ, and ρ. Diffusion coefficients of stable molecules which are structurally close to the radicals (e.g., isobutane or isobutene for *tert*-butyl) are measured or taken from the literature for the conditions of kinetic experiments and used directly. $\sigma = 1/4$ is adopted, since this is

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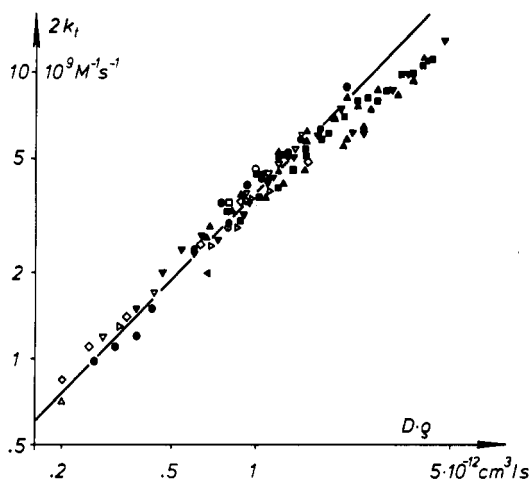(32) Simson, J.; Ponter, A. B. *Can. J. Chem. Eng.* **1975**, *53*, 541.

Figure 3. Selected rate constants for the self-reaction of carbon-centered radicals in liquids: ■, 2-propyl;[34] □, 2-propyl;[23] ●, benzyl;[35] ○, benzyl;[23,36] ◇, hydroxymethyl;[22] ▼, 2-hydroxy-2-propyl;[17] ▽, 2-hydroxy-2-propyl;[26] ⊖, 2,6-dichlorobenzyl;[36] ▷, triethoxysilyloxyethyl;[26] ◁, tert-butoxyacyl;[20] △, tert-butyl;[23] ▲, tert-butyl.[37] Straight line represents $2k_t^s$.

suggested from independent techniques.[33] Finally, ρ is obtained from molecular volumes as the average of the results of various procedures.[12] In Figure 3 we show 96 rate constants for 8 radicals (2-propyl, tert-butyl, benzyl, 2,6-dichlorobenzyl, hydroxymethyl, 2-hydroxy-2-propyl, triethoxysilyloxyethyl, and tert-butoxyacyl) obtained in a variety of solvents and over wide temperature ranges. The straight line is the estimated von Smoluchowski rate constant $2k_t^s$. For $D\rho \leq 2 \times 10^{-12}$ cm^3 s^{-1} the data agree with the prediction within 20%. At higher $D\rho$ there are deviations from which a finite $2k_\infty = 4.3 \times 10^{10}$ M^{-1} s^{-1} can be deduced. We consider this agreement as justification of both the estimation procedure and the diffusion control of the radical self-reaction. Further, it seems safe to state that for our and many related cases of small carbon-centered radicals self-reaction rate constants can be reliably predicted from the classical equation and that the effects stressed in recent theoretical refinements are likely to be rather small and below the present error limits. The simplified equation gives a much poorer agreement (Figure 4), which strengthens the view that it should not be applied to small solute species.

The observation of diffusion control for the self-reaction of small radicals immediately leads to questions about the factors which influence the product distributions. tert-Butyl and 2-hydroxy-2-propyl give both disproportionation and combination products in a ratio of about 7 at room temperature in nonviscous liquids, and for 2-propyl this ratio is about 1. For encounter-controlled reactions it must be governed by processes during encounters. We believe that reorientations in the pairs between repeated collisions play a major role. They are rapid compared to the pair separation by translation. This view is based on the finding that for tert-butyl[38] and 2-hydroxy-2-propyl[17] the disproportionation/combination ratio increases drastically with increasing viscosity or decreasing diffusion coefficient D, whereas for 2-propyl[34] there is no such effect. Re-
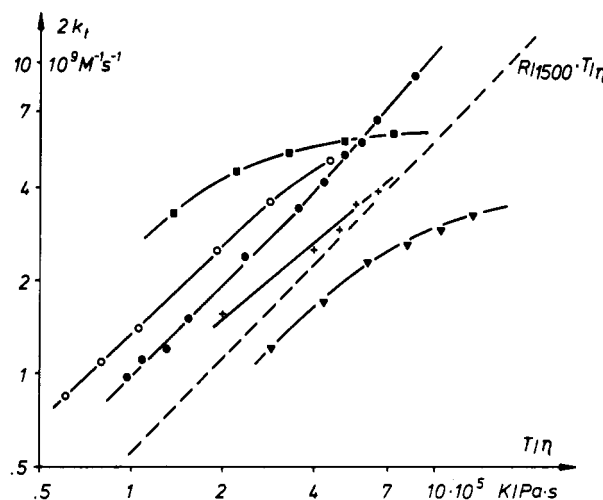
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Figure 4. Rate constants for the self-reaction of radicals vs. T/η: ■, 2-propyl in 3-methyl-3-pentanol;[34] ●, benzyl in toluene;[35] ○, hydroxymethyl in methanol;[22] +, triethoxysilyloxyethyl in tetraethoxysilane;[26] ▼, 2-hydroxy-2-propyl in acetonitrile.[17]
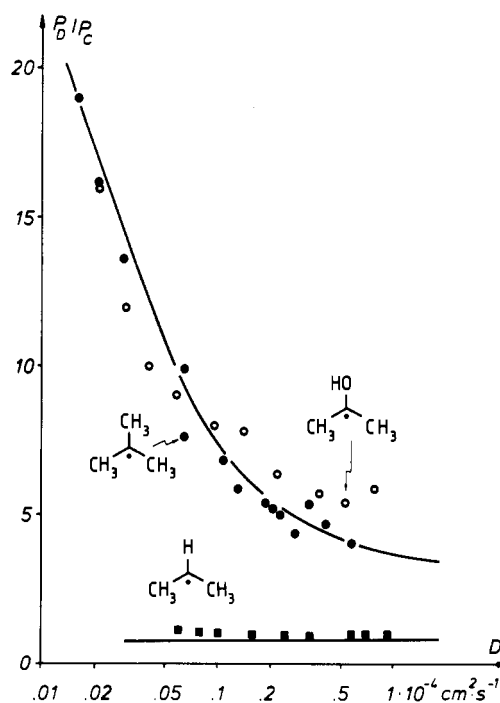

Figure 5. Disproportionation to combination ratios of tert-butyl, 2-hydroxy-2-propyl, and 2-propyl radicals in solution vs. translation diffusion coefficients of model molecules. Curves were calculated. For tert-butyl and 2-hydroxy-2-propyl an average molecular geometry is adopted.

sults are given in Figure 5, which also shows predictions (lines) for the two radical types. For tert-butyl[38] and 2-hydroxy-2-propyl the basis of the effect is as follows: The molecules approximate oblate ellipsoids. Thus, on collision the principal (parallel) axes of two radicals should coincide for formation of a C–C bond by combination. If, now, on the first collision this configuration

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(37) $2k_t$ for 25 °C ≤ T ≤ 50 °C and solvents n-C$_{10}$H$_{22}$, n-C$_{12}$H$_{26}$, n-C$_{14}$H$_{30}$, n-C$_{16}$H$_{34}$, CH$_3$CN, C$_6$H$_6$, (CH$_3$)$_3$COH from ref 12; for 25 °C ≤ T ≤ 80 °C and n-C$_7$H$_{16}$, n-C$_8$H$_{18}$ from unpublished work. Diffusion coefficients are averages of isobutane and isobutene.

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is not achieved, one or both radicals must rotate about a perpendicular axis to meet it. This reorientation of a disk-shaped species is strongly coupled to viscosity since solvent has to be moved away, and consequently, combination is hindered in high viscous liquids. Motions leading to configurations which give disproportionation are less subject to viscous hindrance; i.e., the ratio increases with increasing solvent viscosity.[38] For 2-propyl reorientations favoring the approach to combination and disproportionation geometries are equally influenced by viscosity, and this explains the constant ratio.[34] It is reassuring that the same simple model explains data for at least three radicals. It implies that reorientational motions are considerably faster than translational ones in liquids and have viscosity-independent lower limits of their correlation times. This is well-known[39] but has not yet found recognition by theoreticians, who therefore probably underestimated the degree of averaging of anisotropic reactivities.[30,31]

In the preceding paragraphs we attributed both the rates and the product ratios of the self-reaction of several small radicals solely to transport phenomena. While this concept probably holds for many related species as well, we wish to stress that problems remain and demand further exploration: The origin of the leveling-off in Figure 3 is unclear, and different explanations are possible.[17,40] Effects of radical–solvent associations have been noticed,[17,41] but treatments are controversial. More bulky radicals are known which react in a pseudodiffusive way, and for a variety of these loose radical–radical complexes may lie on the reaction coordinate.[31] Effects of Coulomb repulsions of charged radicals[24,42] have only occasionally been studied. Furthermore, cross-reaction rates of unlike species require further studies, especially in view of the nonexisting basis for the popular cross-termination Ansatz. Thus, plowing the field of radical–radical reactions will certainly disclose more treasures.

The Addition of Nucleophilic Alkyl Radicals to Alkenes

Inter- and intramolecular C–C bond formation by the addition of carbon-centered radicals to unsaturated molecules represents one of the most useful applications of radical chemistry and is of enormous importance for polymer formation.[1] Depending on the type of radical and molecule, the rate constants for this process cover many orders of magnitude.[7] As several recent reviews clarify, they represent a "complex interplay of polar, steric, and bond strength terms" caused by the nature and positions of substituents which can seldom be disentangled, though important trends have been established.[43,44] In a detailed case study we have measured by time-resolved ESR rate constants for the addition
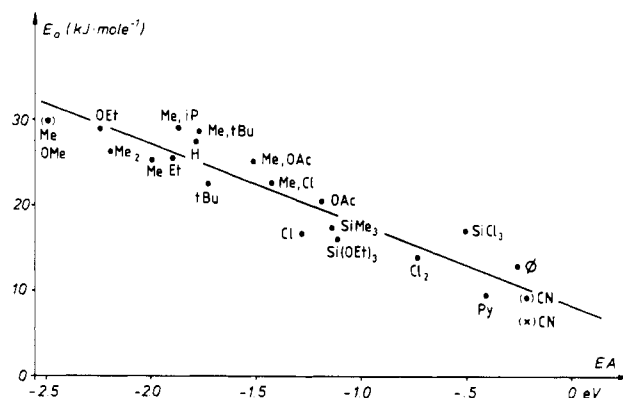

Figure 6. Activation energies for the addition of *tert*-butyl to alkenes CH_2=CR_1R_2 vs. their electron affinities. Data in parentheses are derived from fits with log $(A/M^{-1} s^{-1}) = 7.5$.

of the *tert*-butyl radical, $(CH_3)_3C^\bullet$, to 29 alkenes of type CH_2=CR_1R_2, $ClCH$=CR_1R_2, and CH_3CH=CR_1R_2 with a variety of substituents R_1 and R_2 over wide temperature ranges. The radical was chosen because it has a very low ionization potential, which renders it highly nucleophilic.[15,18,45,46] Therefore, one expects that the polar part of the substituent effects is governed solely by interactions of the radical's SOMO with the olefin's LUMO in the transition state. From simple FMO considerations the activation energy for addition should then decrease with decreasing LUMO energy whereas the rate constant should increase.[47] As a measure of the LUMO energy, one may use the electron affinity of the olefin, and in fact, correlations between rates and electron affinities are already known for other radical reactions.[48]

The results of our case study[2,19,49] are the following: (1) Addition of *tert*-butyl to alkenes is found to occur nearly exclusively at the least substituted carbon. Abstraction from alkyl substituents was observed only for 2,3-dimethyl-2-butene. (2) At 300 K the rate constants cover the wide range from 60 M^{-1} s^{-1} (*cis*-2-butene) to 10^6 M^{-1} s^{-1} (acrylonitrile). (3) The temperature dependence follows the Arrhenius law, and with few irregular exceptions the frequency factors are in the narrow range log $(A/M^{-1} s^{-1}) = 7.5 \pm 0.5$. Thus, the large variation of rate constants is due to changes in the activation energy. So far, the results are as expected from previous experience.[43,44] Moreover, however, (4) for olefins of type CH_2=CR_1R_2 the activation energy E_a and log k depend approximately linearly on the electron affinity of the olefin, and this can be satisfactorily explained in terms of FMO considerations.[2,19] Figure 6 shows the correlation for E_a. Further, (5) for olefins of type $ClCH$=CR_1R_2 and CH_3CH=CR_1R_2 lines with the same slopes but vertically displaced to higher values were found. The displacements quantify the steric effects of α-substituents for the first time: α-Chlorine and α-methyl groups increase the activation energies by 9 and 7.5 kJ/mol, respectively; i.e., a di-

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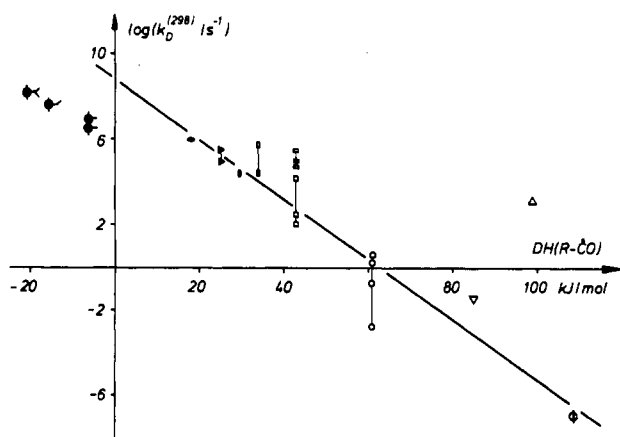
Figure 7. Decarbonylation rates k_D of acyl radicals at 298 K vs. their bond dissociation enthalpies DH(R–CO) for R = C_6H_5 (○),[53] CF_3 (△),[54] c-C_3H_5 (▽),[55] CH_3 (○),[56] C_2H_5 (□),[57](alkyl)CH_2(▣),[57] i-C_3H_7 (□, ■),[34,57] t-C_4H_9 (▶),[33,51] $HOCH_2$ (◕),[51] $HOC(CH_3)_2$ (◐),[17] $C_6H_5CH_2$ (◆),[58] $C_6H_5CHCH_3$ (◆),[58] $C_6H_5C(CH_3)_2$ (◄).[58]

sentanglement of polar (electron affinity) and steric effects has been achieved.

A comparison with relative rate data for other branched nucleophilic alkyl radicals[7,44] leads us to believe that the results 1–6 should also hold for these, at least approximately. For radicals with electron acceptor substituents they will certainly not apply since a correlation of rates and ionization potentials is then expected. In fact, available relative rate data[50] for $\dot{C}H$-$(CN)_2$ support such a correlation, and we are at present carrying out a case study for a similar electrophilic radical. Since the *tert*-butyl case required the accumulation of over 500 individual rate constants, it will take some time before results can be presented.

The Decarbonylation of Acyl Radicals

The rates of decomposition of radicals R–CO into alkyl radicals R· and carbon monoxide determine the success of aldehyde additions to olefins (see Introduction) and the product distribution of the type I cleavage of ketones. For four cases (R· = $(CH_3)_3C$, $(CH_3)_2CH$, $(CH_3)_2COH$, and CH_2OH) we have measured these rates and their temperature dependencies by kinetic ESR and time-resolved NMR.[17,33,34] For others rate data for both gas and liquid phases are available from the literature.[52–58] At room temperature the rate constants

dependent strongly on the nature of R. They cover over 15 orders of magnitude. Therefore, these reactions can serve as versatile unimolecular "radical clock" systems to compete with in relative kinetic measurements.[9,52] The huge order of magnitude effects also hint to a simple and common background effect. This has been found by estimates of the enthalpy changes during the reactions DH(R–CO) by standard thermochemical procedures.[51] Except for the benzyl type radicals the decompositions are endothermic by about 18 (HO-$(CH_3)_2C$–CO) to 109 kJ/mol (C_6H_5–CO). A simple plot of log k vs. DH(R–CO) reveals a linear correlation (Figure 7). The reported frequency factors for the endothermic decarbonylations scatter between 10^{11} and 4×10^{14} s^{-1} with an average value of 10^{13} s^{-1}. This suggests only small entropy changes on the approach to the transition state, so that the large variation in rates is caused by changes in the activation energies. If one adopts 10^{13} s^{-1} for the frequency factors of all endothermic reactions, one obtains for the activation energy $E_a = 26 + 0.80$DH(R–CO) kJ/mol, i.e., a linear Evans–Polanyi relation. Obviously, the rate constants are simply governed by the strength of the bonds to be broken in this case. The slightly exothermic decarbonylations of the phenylacetyl species have somewhat lower frequency factors. This may be explained by a partial stiffening of the torsion about the C_6H_5–$C\dot{C}O$ bond in the transition state, i.e., partial preformation of the conjugated benzyl radical,[58] but there are too few data available to set up correlations which hold for these reactions. In Figure 7 several points deviate markedly from the straight line. These were all obtained by fairly indirect measurements and are subject to criticism.[51] It would be gratifying to see whether future redeterminations with more advanced methods would bring them to closer agreement.

Conclusions

This and previous accounts[9] were written to demonstrate that kinetic ESR spectroscopy is a versatile tool to study mechanisms and rates of many radical reactions in liquids. We have concentrated on the particular feature that large series of rate data can be directly measured within a reasonable amount of time to quite some accuracy and within wide ranges of magnitudes. To be more specific, absolute accuracies of about ±30% are now achievable for well-chosen reaction systems if precautions mentioned above are taken. Self-reactions with rate constants ranging from zero to the diffusion-controlled upper limit are measurable. For radical-molecule reactions the present range of rate constants is about 10–10^6 M^{-1} s^{-1}, and for first-order radical reactions it is about 10–10^5 s^{-1}. For faster radical-molecule or unimolecular radical reactions optical techniques are probably superior. The easy identification of the radical species and the separation of their spectra, however, also allow satisfactory kinetic analyses of fairly complicated reaction schemes. Furthermore, we have presented the results of case studies on the kinetics of three prototypes of radical reactions. The individual data are found in the cited original publications, and only the conclusions obtained from many rate constants were outlined: The self-reaction constants for small

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carbon-centered radicals can be predicted reliably from classical theory, i.e., the von Smoluchowski equation. Electron affinity and/or ionization potentials govern rates of radical additions to olefins and can quantify "polar" effects and be used to separate "steric effects" from these. Finally, bond strengths control the rates of decarbonylation of acyl radicals. In principle, free radical reactions in liquids can be divided into the classes (a) radical–radical self- and cross-reactions, (b) unimolecular fragmentations and rearrangements, and (c) radical–molecule reactions by addition, group or atom transfer, and transfer of electrons. Only for some of these have we presented unifying rationalizations. Of course, much work remains to be done until concepts are available which allow to predict the rate of an arbitrary reaction to some confidence, but we believe that gathering and analyzing data in the spirit of this Account is a path to that goal.