Absolute Rate Constants for the β-Scission and Hydrogen Abstraction Reactions of the *tert*-Butoxyl Radical and for Several Radical Rearrangements: Evaluating Delayed Radical Formations by Time-Resolved Electron Spin Resonance

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Abstract: An analysis is presented for the determination of absolute rate constants for radical transformation reactions in complex reaction systems by time-resolved ESR during intermittent photochemical radical production. The technique is applied to obtain absolute rate constants in large temperature ranges for the β-scission of the *tert*-butoxyl radical in various solvents and its hydrogen abstraction from cyclohexane, cyclopentane, *tert*-butylbenzene, and anisole. Kinetic studies of the neophyl and the 2-methyloxiran-2-yl rearrangements and the decarboxylation of the *tert*-butoxycarbonyl radical also demonstrate the versatility of the method. Further, rate data are given for the addition of the methyl radical to benzene and fluorobenzene, as well as for the hydrogen abstraction of methyl from di-*tert*-butyl peroxide.

Introduction

Reactions which convert transient radicals $A\cdot$ into other forms $B\cdot$ are ubiquitous. They include conformational and configurational isomerizations, structural rearrangements by internal atom, and group migrations or cyclizations, fragmentations, and bimolecular reactions by electron, atom, or group transfer as well as additions to unsaturated compounds. Many of these processes are synthetically and technically useful, and hence, much effort has been devoted to determine their rate constants both in the gas and in the liquid phase.[1] Depending on radical and reaction, the rate constants vary by many orders of magnitude. Ideally, for their determination one would apply kinetic isolation conditions, that is, generate the primary species $A\cdot$ in a short pulse and then follow its conversion to $B\cdot$ by a spectroscopic technique, eventually in competition with the formation of an indicator radical. However, most direct detection techniques require appreciable initial radical concentrations of about 10^{-6}–10^{-5} M. For transient radicals the bimolecular self- and cross-terminations are close to diffusion or collision control ($2k_t \approx (1-10) \times 10^9$ M^{-1} s^{-1} for usual conditions),[1c] and thus interfere with the radical transformation in times longer than about $10-1000$ μs after the pulse. Hence, the reactions of interest can only be isolated if the rate constants are fairly large.

Lower rate constants can be derived from the time dependence of the radical concentrations in kinetic systems with competing reactions. Then, all competing reactions must be known, and the time profiles must be sufficiently exact so that several rate parameters can be extracted simultaneously by numerical fits of rate equations to the experimental data. Here, as in previous work, we use this technique in combination with radical detection by electron spin resonance. Transient radicals are produced photochemically from suitable precursors with intermittent generation. Kinetic traces of their concentrations are taken during the on- and off-periods, are coherently accumulated to increase the signal-to-noise ratio, and are analyzed. Full analyses of the complete traces are possible but tedious and were performed earlier for a fragmentation[2a] and several hydrogen abstractions[2b] competing with self- and cross-terminations. However, a simpler analysis is sufficient if the desired radicals $B\cdot$ are formed rapidly from $A\cdot$ or other precursors, and if their first- or pseudo-first-order reactions contribute only little to the total decay; that is, they are slow compared to the terminations. Then, the rate parameters follow from fits of approximate analytical formulas to the decay profiles in the off-period of radical generation. This procedure yielded rate constants for various hydrogen and chlorine atom transfer reactions[3] and radical additions to alkenes, alkynes, and aromatic compounds.[4]

(1) (a) Kerr, J. A.; Moss, S. J. *Handbook of Bimolecular and Termolecular Gas Reactions*; CRC Press: Boca Raton, FL, 1981, Vol. 1, p 2. (b) de Mayo, P. *Rearrangement in Ground and Excited States*; Academic Press: New York, 1980, Vol. 1−3. (c) Landolt-Börnstein, *Radical Reaction Rates in Liquids*; Fischer H., Ed.; New Series, Springer: Berlin, Germany, 1983−1997, Vol. II/13, II/18. (d) Baulch, D. L.; Cobos, C. J.; Cox, R. A.; Esser, C.; Frank, P.; Just, T.; Kerr, J. A.; Pilling, M. J.; Troe, J.; Walker, R. W.; Warnatz, J. *J. Phys. Chem. Ref. Data* **1992**, *21*, 411−734. (e) Baulch, D. L.; Cobos, C. J.; Cox, R. A.; Frank, P.; Hayman, G.; Just, T.; Kerr, J. A.; Murrells, T.; Pilling, M. J.; Troe, J.; Walker, R. W.; Warnatz, J. *J. Phys. Chem. Ref. Data* **1994**, *23*, 847−1033. (f) Neta, P.; Grodkowski, J.; Ross, A. B. *J. Phys. Chem. Ref. Data* **1996**, *25*, 709−1050. (g) Fossey, J.; Lefort, D.; Sorba, J. *Free Radicals in Organic Chemistry*; John Wiley & Sons: New York, 1995. (h) Scaiano, J. C. *CRC Handbook of Organic Photochemistry*; CRC Press: Boca Raton, FL, 1989, Vol. I, II.

(2) (a) Rüegge, D.; Fischer, H. *Int. J. Chem. Kinet.* **1986**, *18*, 145−158. (b) Rüegge, D.; Fischer, H. *J. Chem. Soc., Faraday Trans. 1* **1988**, *84*, 3187−3205.

(3) (a) Dütsch, H.-R.; Fischer, H. *Int. J. Chem. Kinet.* **1981**, *13*, 527−541. (b) Dütsch, H. R.; Fischer, H. *Int. J. Chem. Kinet.* **1982**, *14*, 195−200.
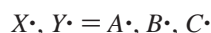
(4) (a) Fischer, H. in *Free Radicals in Biology and Environment*; Minisci, F., Ed.; Kluwer Academic Publishers: Dordrecht, The Netherlands, 1997l; pp 63−78 and references given therein. (b) Rubin, H.; Fischer, H. *Helv. Chim. Acta* **1996**, *79*, 1670−1682. (c) Zytowski, T.; Fischer, H. *J. Am. Chem. Soc.* **1996**, *118*, 437−439. (d) Zytowski, T.; Fischer, H. *J. Am. Chem. Soc.* **1997**, *119*, 9, 12869−12878. (e) Weber, M.; Fischer, H. *Helv. Chim. Acta* **1998**, *81*, 770−780.

Now, we extend this analysis to cases where the observed species are formed not only during the photolysis but also thereafter from an instantly formed precursor. Then, in the beginning of the off-period the concentration vs time profiles have a sigmoid shape. This effect of delayed radical formation was already observed by Bennett et al.[5] in 1974. However, it has not yet been exploited to obtain rate constants for radical reactions.

In the following, we provide the appropriate analytical formulas in short. These are then applied to the formation of the methyl radical by β-scission of the *tert*-butoxyl radical and to its competing hydrogen abstraction reactions from several substrates. These reactions are well-known[1] but especially, for the β-scission reliable absolute rate constants, are still missing. To show the versatility of the method, we also restudy several radical rearrangements. Moreover, rate data are given for processes which accompany the reactions of major interest.

Reaction Kinetics

We consider the sequence of reactions 1−4 which corresponds to the studied systems

$$\text{source} \xrightarrow{I} A\cdot \tag{1}$$

$$A\cdot \xrightarrow{k_A} B\cdot \tag{2}$$

$$B\cdot \xrightarrow{k_B} C\cdot \tag{3}$$

$$X\cdot + Y\cdot \xrightarrow{2k_t} \text{products} \tag{4}$$

$$X\cdot, Y\cdot = A\cdot, B\cdot, C\cdot$$

In the on-period of photolysis, radical $A\cdot$ is produced from a suitable precursor with a constant rate I (1). It then transforms to radical $B\cdot$ by a first- or pseudo-first-order process 2 with rate constant k_A. Radical $B\cdot$, in turn, reacts with first- or pseudo-first-order kinetics in reaction 3 to radical $C\cdot$ (rate constant k_B). All radicals self- and cross-terminate to nonradical products (4). The rate constants of these termination reactions are assumed to be equal, and deviations therefrom are considered below. Further, the radicals shall reach their steady-state concentrations in the on-period. The rate equations for reactions 1−4 yield for the steady state

$$[A\cdot]_0 + [B\cdot]_0 + [C\cdot]_0 = \sqrt{\frac{I}{2\,k_t}} = I\cdot\tau_2 \tag{5}$$

where $\tau_2 = (2\,k_t([A\cdot]_0 + [B\cdot]_0 + [C\cdot]_0))^{-1}$ is the second-order lifetime of the total radical concentration, and

$$[A\cdot]_0 = \frac{I\cdot\tau_A}{1 + \tau_A/\tau_2} \tag{6}$$

$$[B\cdot]_0 = \frac{I\cdot\tau_B}{(1 + \tau_A/\tau_2)\cdot(1 + \tau_B/\tau_2)} \tag{7}$$

$$[C\cdot]_0 = [B\cdot]_0\cdot\tau_2/\tau_B = \frac{I\cdot\tau_2}{(1 + \tau_A/\tau_2)\cdot(1 + \tau_B/\tau_2)} \tag{8}$$

where $\tau_A = k_A^{-1}$ and $\tau_B = k_B^{-1}$. Equations 6−8 are useful to extract relative lifetimes from steady-state radical concentrations and have widely been applied.[1c] For the off-period starting at $t = 0$ one obtains the following:

$$[A\cdot] = [A\cdot]_0\cdot\frac{e^{-t/\tau_A}}{1 + t/\tau_2} \tag{9}$$

$$[B\cdot]_0 = \frac{[B\cdot]_0}{1 + t/\tau_2}\left\{e^{-t/\tau_B} + \tau_A\cdot(1 + \tau_B/\tau_2)\cdot\frac{e^{-t/\tau_A} - e^{-t/\tau_B}}{\tau_A - \tau_B}\right\} \tag{10}$$

$$[C\cdot] = \frac{[C\cdot]_0}{1 + t/\tau_2}\left\{1 + \frac{\tau_B}{\tau_2}\cdot(1 - e^{-t/\tau_B}) + \frac{\tau_A}{\tau_2}\cdot(1 + \tau_B/\tau_2)\left(\frac{\tau_B\cdot e^{-t/\tau_B} - \tau_A e^{-t/\tau_A}}{\tau_A - \tau_B} + 1\right)\right\} \tag{11}$$

In the following we concentrate on the behavior of radical $B\cdot$ and on the determination of its formation (τ_A) and decay (τ_B) parameters with eq 10. When $A\cdot$ converts instantly to $B\cdot$, this simplifies to the previously used relation[3,4]

$$[B\cdot] = [B\cdot]_0\frac{e^{-t/\tau_B}}{1 + t/\tau_2} \tag{12}$$

For a fast conversion obeying $\tau_A \ll \tau_B$ and $1 + \tau_A/\tau_B \approx (1 - \tau_A/\tau_B)^{-1} \approx e^{\tau_A/\tau_B}$, it can be rewritten for $t \gg \tau_A$ as

$$[B\cdot] = [B\cdot]_0\frac{e^{-(t-\tau_A)/\tau_B}}{1 + (t - \tau_A)/(\tau_2 + \tau_A)} \tag{13}$$

In essence, this relation was applied earlier to determine the fragmentation rate constant of the cumyloxyl radical.[4d] For a pure second-order decay of $B\cdot$ it becomes

$$[B\cdot] = \frac{[B\cdot]_0}{1 + (t - \tau_A)/(\tau_2 + \tau_A)} \tag{14}$$

Basically, eqs 13 and 14 show that a sufficiently fast delayed formation causes a simple shift of the onset of the radical decay by the precursor lifetime τ_A.

To check the influence of unequal terminations on rate constants k_A and k_B obtained by fits of eq 10 to experimental data, we solved the rate equations for reactions 1−4 numerically[6] for $I = 10^{-3}$ M s^{-1}, $2k_t^B = 10^9$ M^{-1} s^{-1}, 10^3 s$^{-1} \le k_A \le 10^5$ s^{-1}, 10 s$^{-1} \le k_B \le 200$ s^{-1}, and $2k_t^{AA}$ and $2k_t^{CC}$ set as 2×10^8 M^{-1} s^{-1} and/or 5×10^9 M^{-1} s^{-1} using the geometric mean[7a] for the cross-terminations. The fits to the numerical results retrieved the inputs k_A and k_B with less than 20% deviations for most cases and a maximum deviation of about a factor of 2 for extremely different termination constants. Hence, if the radicals have similar sizes and terminate diffusion-controlled, that is, have similar termination constants in the order of magnitude of $1-10 \times 10^9$ M^{-1} s^{-1} for usual solvent viscosities, applications of eq 10 to kinetic traces should provide rather reliable results. For the carbon-centered radicals encountered in this work, this is expected to be well fulfilled,[7b] and there is some evidence that the self-termination constant of the *tert*-butoxyl radical occurs also with a rate close to the diffusion-controlled limit.[1c]

Experimental Section

Most of the chemicals were obtained commercially in the purest available forms and used as received. Water, *tert*-butylbenzene, and di-*tert*-butyl peroxide were purified by repeated distillation. Benzene,

(5) Bennett, J. E.; Eyre, J. A.; Rimmer C. P.; Summers, R. *Chem. Phys. Lett.* **1974**, *26*, 69−71.

(6) *MATLAB 4.2c.1* using the Gear algorithm for integrating the stiff differential equations. To take account of the closure condition in the repetitive sampling, we repeated the integrations several times and, for each repetition, we set the initial concentrations to the final concentrations of the previous one. The method converged after three to four iterations.

(7) (a) Paul, H.; Segaud, C. *Int. J. Chem. Kinet.* **1980**, *12*, 637−647. (b) Fischer, H.; Paul, H. *Acc. Chem. Res.* **1987**, *20*, 200−206.

fluorobenzene, cyclopentane, and cyclohexane were passed through an alumina column, and all solutions were freed from oxygen by at least 30 min of purging with argon or helium before use. The arrangements and procedures for steady-state and time-resolved electron spin resonance spectroscopy have been described earlier.[2-4] In principle, the signal s(n) of a radical is monitored with repetition times of 5−10 ms. Individual signal vs time profiles (100000−500000) are coherently accumulated and provide 500 data points in the n channels of a transient recorder. The s(n) obey s(n) = c[R(t)], with [R(t)] representing the radical concentration at time $t = n\tau$. Here, τ is the channel time width and c is a sensitivity constant which has not been determined since it does not influence the extraction of first-order rate constants.

The decay parts of the time profiles were analyzed by fits using the simplex algorithm and either eq 9 if radical $A\cdot$ was observed, eq 12 or 9 if the transformation to $B\cdot$ was very fast, or eq 10. The fitting procedure required the definition of the effective time t_0 at which the photochemical radical generation ends. Actually, the sector edge does not cut off the light beam instantly but in a sigmoid type fashion[2] extending over 10−20 μs. This variation was measured by recording the signal amplitude of *tert*-butyl radicals during continuous photolysis of 4 vol % di-*tert*-butyl ketone in tetradecane and at room temperature as a function of the sector angle position ϕ. In this system, *tert*-butyl is generated in about 1−2 μs after ketone excitation, that is, practically instantly,[8] and shows a pure second-order decay.[9] Hence, the square of the signal amplitude is proportional to the generation rate I. In the transition region from the on- to the off-period, this rate followed the relation $I(\phi) \propto (1 - \tanh[b(\phi - \phi_0)])/2$, where ϕ_0 is the (arbitrarily set but fixed) origin of the angular scale and the parameter b depends on the slit width. t_0 was then defined by the position of the inflection point ϕ_0 and was determined in kinetic experiments involving the di-*tert*-butyl ketone system and simulations of the *tert*-butyl trace including the sigmoid generation. Interestingly, the location of the inflection point resulted also and more simply from fits of pure second-order decays to eq 15

$$[B\cdot] = \frac{[B\cdot]_0}{1 + (t - t_0)/\tau_2} \quad (15)$$

which is very similar to eq 14. This is not surprising, since the sigmoid drop of the radical generation and a delayed formation of the radical from its precursor must lead to a similar behavior of the concentration in the on−off transition region. Hence, t_0 was mostly determined by the simpler procedure. In analyses of the various kinetic experiments, t_0 was taken as time origin and defined the channel number for the on−off transition. This number was held constant as long as the optical arrangement remained unchanged. More details justifying the procedures are given as Supporting Information. The upper limiting value of a first- or pseudo-first-order rate constant k_A measurable with the technique is about 10^5 s^{-1}. Rate constants given in the figures and tables are averages from 5 to 15 individual determinations. ESR spectra obtained during continuous photolysis demonstrate the reactions and are included in the Supporting Information, and all radicals mentioned were identified by their known g factors and hyperfine coupling constants.

β-Scission and Hydrogen Abstractions of the tert-Butoxyl Radical and Reactions of the Methyl Radical with Solvents

The β-scission of the *tert*-butoxyl radical into acetone and the methyl radical is well-known.[1] In liquids it often occurs in competition with hydrogen abstraction by *tert*-butoxyl from solvent or substrates. Early extensive product studies on the ratio of rate constants for the β-scission and for the hydrogen abstraction from cyclohexane and other substrates in various

solvents were presented by Walling and co-workers.[10] They found an astonishing large variation with the solvent and concluded that this is due to a solvent dependence of the fragmentation and not of the hydrogen abstraction. Later, similar product studies provided many rate constants for addition and abstraction processes of the *tert*-butoxyl radical relative to the β-scission and/or the hydrogen abstraction from cyclohexane and other donors.[1c]

The strong solvent dependence of the β-scission and the solvent independence of the hydrogen abstraction reaction were confirmed more recently by Ingold et al.[11] in direct time-resolving studies of product formation and radical decay at 30 °C. These authors also discussed the solvent dependence in detail but used the cumyloxyl radical as the model alkoxyl because *tert*-butoxyl decayed too slowly for their optical detection methods. Since our technique allows the study of slower processes, we applied it here to *tert*-butoxyl and also present the temperature dependence of the rate constants. The *tert*-butoxyl radical cannot be directly detected in the liquid phase by electron spin resonance.[12] Therefore, the kinetic probe is the methyl radical and its delayed formation from *tert*-butoxyl after the scission reaction. 1,1,2-Trichloro-1,2,2-trifluoroethane (Frigen 113), benzene, and fluorobenzene were used as fairly inert solvents, and the *tert*-butoxyl radicals were generated by photolysis of 10 vol % di-*tert*-butyl peroxide. The dissociative excited state of the peroxide ensures an instant *tert*-butoxyl formation. As further medium, neat di-*tert*-butyl peroxide was employed. It is known that *tert*-butoxyl abstracts a hydrogen atom from the peroxide. The resulting radical $\cdot$CH$_2$CMe$_2$-OOCMe$_3$ undergoes rapid fragmentation to 2,2-dimethyl oxirane and *tert*-butoxyl with $k_r = 7 \times 10^5$ s^{-1} at 298 K in benzene.[13] Since this reaction regenerates *tert*-butoxyl and is fast in the temperature range employed here, it should not influence the methyl formation kinetics.

In accord with expectation, ESR spectra taken during continuous photolysis of the peroxide in the four solvents revealed the presence of methyl in high predominance. Solvent-derived radicals and the peroxide-derived species $\cdot$CH$_2$CMe$_2$-OOCMe$_3$ were not observed, but there were very weak signals of radicals which are formed from products of the major reactions. Thus, the acetonyl radical $\cdot$CH$_2$COCH$_3$ arises by hydrogen abstraction from the scission product acetone, the 2-hydroxyprop-2-yl radical (CH$_3$)$_2$$\dot{C}$OH by photoreduction of acetone, and the *tert*-butoxymethyl radical, $\cdot$CH$_2$CO(CH$_3$)$_3$, by hydrogen abstraction from the cross-termination product of methyl and *tert*-butoxyl. The total concentration of the additional radicals was less than about 8% of methyl and was neglected in the analysis.

Figure 1 shows kinetic traces of the methyl radical in Frigen 113 containing 10 vol % di-*tert*-butyl peroxide at two temperatures. Overlayed are fits of eq 10 to the data, and the bottom traces are the fit residuals. After the end of the photolysis the delayed formation of methyl is clearly visible, in particular in the enlarged inset. Table 1 gives the lifetimes obtained from

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(10) (a) Walling, C.; Pawda, A. *J. Am. Chem. Soc.* **1963**, *85*, 1593−1597. (b) Walling, C.; Pawda, A. *J. Am. Chem. Soc.* **1963**, *85*, 1597−1601. (c) Walling, C.; Wagner, P. *J. Am. Chem. Soc.* **1963**, *85*, 2333−2334. (d) Walling, C.; Wagner, P. J. *J. Am. Chem. Soc.* **1964**, *86*, 3368−3375. (e) Walling, C. *Pure Appl. Chem.* **1967**, *15*, 69−80, and further references therein.

(11) Avila, D. V.; Brown, C. E.; Ingold, K. U.; Lusztyk, J. *J. Am. Chem. Soc.* **1993**, *115*, 466−470.

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(13) Bloodworth, A. J.; Davies, A. G.; Griffin, I. M.; Muggleton, B.; Roberts, B. P. *J. Am. Chem. Soc.* **1974**, *96*, 7599−7601.
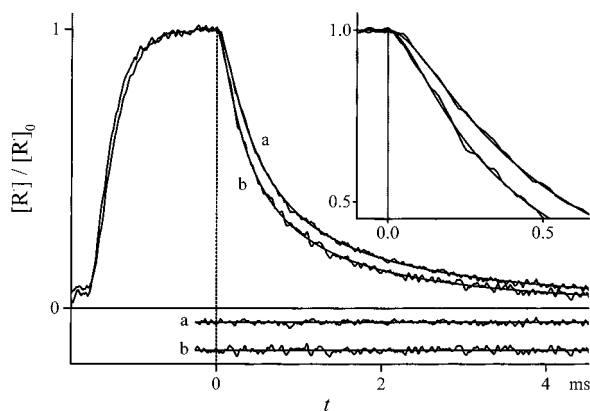
Figure 1. Methyl concentrations vs time in Frigen 113 at (a) 298 ± 1 K and (b) 307 ± 1 K and fits of eq 10 to the data. Bottom traces are residuals of fits, and the inset shows an expansion of the traces around $t = 0$ s.

Table 1. Lifetimes τ_2, τ_A, and τ_B Obtained by Fits of Equation 10 to Kinetic Traces of the Methyl Radical in Frigen 113 at Different Temperatures[a]

T, K	τ_2, μs	τ_A, μs	τ_B, ms
278	424 (50)	394 (23)	60 (20)
283	409 (51)	338 (30)	33 (8)
289	383 (31)	215 (11)	23 (10)
293	374 (24)	164 (9)	17 (2)
298	370 (19)	125 (6)	14 (2)
302	363 (19)	85 (3)	11 (3)
307	350 (32)	59 (2)	8.3 (2)

[a] Standard deviations are given in brackets in units of the last quoted digit.

the fits. Obviously, several lifetimes are significant, are of similar orders of magnitude, and can be determined simultaneously, though with different confidence. The second-order lifetime τ_2 is due to terminations and is not evaluated here. τ_A is interpreted as the lifetime of *tert*-butoxyl, and since no solvent-derived radicals are observed, it is identified as the inverse rate constant of the β-scission. τ_B reflects reactions of the methyl radical with some constituent of the Frigen 113 solution. It was found that τ_B^{-1} increases linearly with the concentration of di-*tert*-butyl peroxide and passes through the origin of a corresponding pseudo-first-order plot, whereas τ_A decreases only very slightly. Hence, the reaction leading to τ_B is very probably and exclusively the hydrogen abstraction of methyl from the peroxide. From the slope of the pseudo-first-order plot, we obtained $k_{Me,298} = 132(37)$ M^{-1} s^{-1}, and experiments at different temperatures gave $\log(k_{Me}/$ M^{-1} s$^{-1}) = 9.3(3) - 41.0(15)/2.303RT$ with the activation energy expressed in kilojoules per mole and standard deviations given in units of the last quoted digit. The frequency factor is in the normal range for hydrogen atom abstractions, and the rate constants are small enough to be compatible with the undetectably low concentration of ·CH$_2$CMe$_2$OOCMe$_3$.

Kinetic traces taken with the other solvents benzene, fluorobenzene, and neat di-*tert*-butyl peroxide closely resembled those given in Figure 1. For benzene and fluorobenzene, the lifetime τ_B was shorter than predicted by the reaction of methyl with the peroxide alone. This is due to the well-known methyl addition to aromatic compounds. From τ_B the rate constants k_{add} of this process were obtained using $\tau_B^{-1} = k_{DTBPO}[peroxide] + k_{add}[solvent]$ with k_{DTBPO} as given above. In Arrhenius form they are presented by $\log(k_{add}(benzene)/M^{-1} s^{-1}) = 8.3(2) - 36.7(10)/2.303RT$ and $\log(k_{add}(fluorobenzene)/M^{-1} s^{-1}) = 8.7(7) - 39.5(2)/2.303RT$, in excellent agreement with our earlier data.[4d]
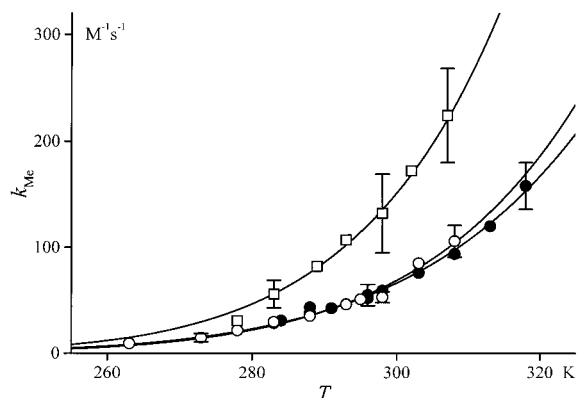

Figure 2. Rate constants and fits to the Arrhenius equation for the reaction of methyl radicals with benzene (closed circles) and fluorobenzene (open circles) and di-*tert*-butyl peroxide in Frigen 113 (open squares).
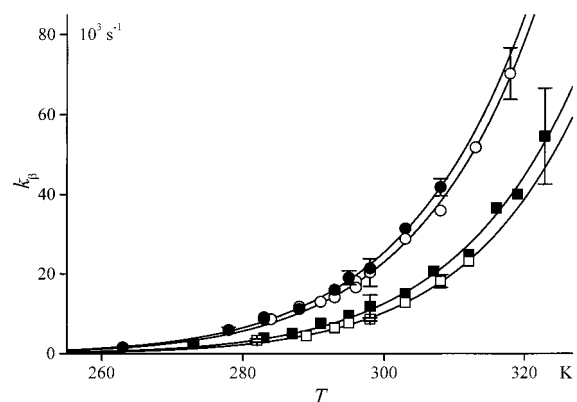

Figure 3. Rate constants and fits to the Arrhenius equation for the β-scission of the *tert*-butoxyl radical in Frigen 113 (open squares), di-*tert*-butyl peroxide (closed squares), benzene (closed circles), and fluorobenzene (open circles).

Table 2. Absolute Rate Constants and Arrhenius Parameters for the β-Scission of the *tert*-Butoxyl Radical[a]

solvent	T, K	$k_{\beta,298}$, s^{-1}	E_a, kJ/mol	$\log(A/s^{-1})$
Frigen 113	278–312	8050 (400)	52.7 (19)	13.2 (5)
DTBPO	283–323	12000 (2900)	50.5 (18)	12.9 (5)
C$_6$H$_6$	284–318	20300 (3500)	48.7 (9)	12.8 (2)
C$_6$H$_5$F	263–308	21400 (1800)	47.5 (11)	12.7 (3)

[a] Standard deviations are given in brackets in units of the last quoted digit. DTBPO = di-*tert*-butyl peroxide.

Figure 2 shows the temperature dependence of the rate constants for the reactions of the methyl radical with the solvents.

The temperature dependence of the rate constants k_β for the β-scission of the *tert*-butoxyl radical is shown in Figure 3, and the activation parameters are given in Table 2. As concluded by Walling et al. for *tert*-butoxyl[10] and found by Ingold et al. for cumoxyl,[11] k_β varies with the solvent and for our solvents at room temperature by a factor of 2.6. The frequency factors are normal for the elimination of a small group, and the above-mentioned decrease of τ_A with increasing peroxide concentration is explained by the increasing scission rate.

Reliable absolute values for k_β of *tert*-butoxyl in liquid media are still missing. From relative values k_β/k_H and various absolute rate constants for the hydrogen abstraction k_H, Scaiano[14a] deduced $k_\beta = 29\,000$ s^{-1} for 295 K and aromatic solvents. This is strongly supported by our findings. Wong's[14b] estimate of $k_\beta = 300$ s^{-1} in di-*tert*-butylperoxide at room temperature is much too low, and Ingold's[14c] early Arrhenius parameters also lead

to very small values. For aqueous solution and at room temperature, Bors et al.[14d] reported $k_\beta = 1.4 \times 10^6$ s^{-1}. This is larger than our data but compatible with an earlier estimate of $10^6 < k_\beta < 10^7$ s^{-1} by Gilbert et al.[14e] If the data for the aqueous phase are correct, the solvent dependence is even larger than indicated by the results found for organic solvents alone. Gas-phase rate constants are also available. By a combination of earlier data, Choo and Benson[15] obtained log(A/s^{-1}) = 14.1 and E_a = 64 kJ/mol. Using a calculated frequency factor for the combination of *tert*-butoxyl with NO, Batt et al.[16] determined log(A/s^{-1}) = (14.04 ± 0.37) and E_a = (62.5 ± 0.6) kJ/mol for 303−443 K. The rate constants at 300 K are at least 10 times smaller in the gas phase than in solution, and both the frequency factors and the activation energies are significantly lower for the liquid phase. The lower activation energies point to considerable solvation effects, which are already clear from the solvent dependence. They are likely due to the fact that the transition state for the β-scission from the unpolar radical to the polar acetone is more polar than the radical. Hence, it is more stabilized by interactions with polar and polarizable solvents than the radical. Our small selection of solvents does not allow us to quantify this point, and we refer to the earlier discussions.[10,11] Further, the lower activation energies for the solutions may also mean earlier transition states, and this may lead to the lower frequency factors. Our data in Table 2 confirm this correlation of the activation parameters. In comparison to cumyloxyl[11] the β-scission of *tert*-butoxyl is about a factor of 20 slower at 30 °C, in agreement with known structural effects on the cleavage.[10]

In inert solvents the hydrogen abstraction reaction of the *tert*-butoxyl radical with suitable added substrates will compete with the β-scission. If not too fast, its rate constant can also be determined using eq 10. In principle, one can kinetically follow either the substrate-derived species or the methyl radical. In both cases the lifetime τ_A obeys $\tau_A^{-1} = k_\beta + k_H[\text{substrate}]$, where k_β is the rate constant for the β-scission. The choice of the radical will depend on the ease of its detection.

Here, we investigate the hydrogen abstractions from cyclohexane, cyclopentane, *tert*-butylbenzene, and anisole. For all of these substrates, the radical formed by the hydrogen abstraction was observed besides methyl. Methyl has less ESR-line groups than the cycloalkyl species but more than the primary radicals from *tert*-butylbenzene and anisole. Therefore, in the first two cases, methyl was followed whereas in the latter the kinetics of the substrate-derived radicals was analyzed.

Cyclohexane was added in 11.5 and 24.4 mM concentrations to solutions of di-*tert*-butyl peroxide (10 vol %) in Frigen 113, benzene, and fluorobenzene. Plots of τ_A^{-1} vs the cyclohexane concentrations were linear. Experiments at different temperatures led to the data shown in Figure 4, and the activation parameters of the abstraction constant for the individual solvents are given in Table 3.

For the three solvents the rate constants are nearly equal, and the fit of one Arrhenius equation to the combined data shown
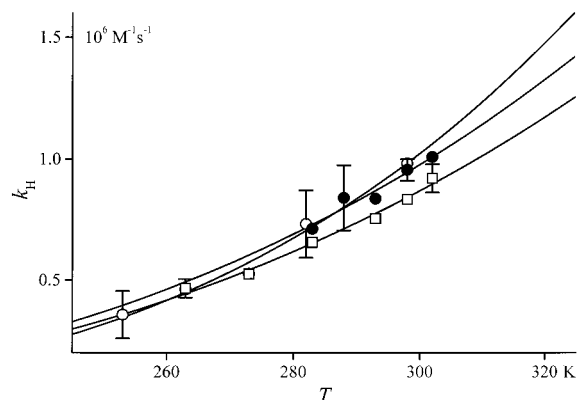

Figure 4. Rate constants and fits to the Arrhenius equation for the hydrogen abstraction of the *tert*-butoxyl radical from cyclohexane in Frigen 113 (open squares), benzene (closed circles), and fluorobenzene (open circles).

in Figure 4 renders the small differences of the activation parameters insignificant. This again supports Walling's and Ingold's conclusion[10,11] of solvent-independent abstractions. Moreover, our absolute rate constants and activation parameters agree very well with the few previous data. Thus, Howard and Scaiano[17a] report an absolute value of $k_H = 1.6 \times 10^6$ M^{-1} s^{-1} at 300 K whereas we find about 1.0×10^6 M^{-1} s^{-1}. For Frigen 113, benzene, and fluorobenzene, Walling's relative data[10] led to $E_{a,\beta} - E_{a,H}$ = 40.0, 36.2, and 32.8 kJ/mol and log(A_β/A_H/M) = 5.04, 4.63, and 4.15, and our absolute data yield $E_{a,\beta} - E_{a,H}$ = 40.8, 36.8, and 32.9 kJ/mol and log(A_β/A_H/M) = 5.2, 4.7, and 4.2. Further, we note that the rate constants for hydrogen abstraction from cyclohexane are very similar for *tert*-butoxyl and cumyloxyl radicals[11] (9.1×10^5 vs 1.2×10^6 M^{-1} s^{-1} at 30 °C); that is, there are only small structural effects of the alkoxyl radical residues on the hydrogen abstraction.[10,11] Our rate constants k_H also provide a coarse re-estimate of the self-termination constant $2k_t$ of the *tert*-butoxyl radical at about room temperature and in low viscous solvents from known ratios $2k_t/k_H^2$. Walling et al.[17b] reported $2k_t/k_H^2 = 0.01$, which leads to an acceptable $2k_t \approx 10^{10}$ M^{-1} s^{-1}. Ingold's $2k_t/k_H^2 = 0.35$[14c] gives a value that is too high, but both results confirm a fast self-termination.

The same procedure was applied to the hydrogen abstraction of *tert*-butoxyl from cyclopentane (22−124 mM) in fluorobenzene and provided the rate parameters also displayed in Table 3. For this substrate various absolute hydrogen abstraction rate constants are available,[18] and a comparison of our data shows again good general agreement.

For *tert*-butylbenzene (1.0−5.2 M) and methylphenyl ether (anisole, 0.5−1.5 M) in di-*tert*-butyl peroxide, the kinetic traces of the substrate-derived primary radicals were analyzed. As before, plots of τ_A^{-1} vs the substrate concentrations were linear. The rate constants k_H and the activation parameters (Table 3) again agree with some earlier data. The hydrogen abstraction from *tert*-butylbenzene was measured in benzene relative to the β-scission.[19] With k_β from Table 2 the reported ratios convert to $k_H = 1.8 \times 10^4$ M^{-1} s^{-1} at 313 K[19a] and to $k_H = 8.8 \times 10^4$

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Table 3. Absolute Rate Constants k_H and Arrhenius Parameters for the Hydrogen Abstraction of the *tert*-Butoxyl Radical from Different Substrate[a]

substrate	solvent	T, K	$k_{H,298}$, $M^{-1}s^{-1}$	E_a, kJ/mol	$\log(A/\,M^{-1}s^{-1})$	ref
C_6H_{12}	Frigen 113	263–302	8.3 (5) × 10⁵	11.9 (7)	8.0 (2)	
	C_6H_6	283–302	9.6 (5) × 10⁵	12.1 (19)	8.1 (6)	
	C_6H_5F	253–298	9.8 (12) × 10⁵	14.6 (11)	8.5 (2)	
	average			13.0 (10)	8.2 (2)	
C_5H_{10}	C_6H_5F	253–298	7.2 (17) × 10⁵	14.8 (7)	8.5 (1)	
	DTBPO	295	8.8 × 10⁵			18a
	DTBPO or C_6H_6	253–303	4.3 × 10⁵ [b]	25.5 (13)	10.1 (2)	18b
	DTBPO/C_6H_6	236–344	8.5 × 10⁵ [b]	14.5 (25)	8.5 (5)	18c
	C_6H_6	298	10.7 × 10⁵			18d
	c−C_3H_6	149–216	12.8 × 10⁵ [b]	14.8 (15)	8.7 (3)	18e
	CF_2CCl_2	150–205	10.6 × 10⁵ [b]	14.7 (15)	8.6 (3)	18e
$C_6H_5C(CH_3)_3$	$C_6H_5C(CH_3)_3$	247–283	3.9 × 10⁴ [b]	25.7 (25)	9.1 (8)	
$C_6H_5OCH_3$	DTBPO	231–293	9.5 × 10⁴ [b]	21.8 (8)	8.8 (2)	
		253–303	9.3 × 10⁴ [b]	24.7 (13)	9.3 (2)	18b

[a] Standard deviations are given in brackets in units of the last quoted digit. DTBPO = di-*tert*-butyl peroxide [b] From the Arrhenius parameters.

M^{-1} s^{-1} at 318 K,[19b] whereas we find $k_{H,313} = 6.5 \times 10^4$ M^{-1} s^{-1} and $k_{H,318} = 7.6 \times 10^4$ M^{-1} s^{-1}. For anisole, Wong[18b] also measured rate constants k_H directly which are close to ours (Table 3). Further, Schwetlick et al.[20a] obtained a ratio of the rate constants for hydrogen abstraction and β-scission of 0.235 M^{-1} in anisole at 408 K. Assuming that k_β is the same in anisole as in fluorobenzene, the ratio yields $k_{H,408} = 9.8 \times 10^5$ M^{-1} s^{-1}, which is equal to our prediction of $k_{H,408} = 10.2 \times 10^5$ M^{-1} s^{-1}. Sakurai et al.[20b] reported the same ratio in Frigen 113 as 6.0 M^{-1} at 318 K, which leads to $k_{H,318} = 2.1 \times 10^5$ M^{-1} s^{-1}, also very similar to our result $k_{H,318} = 1.7 \times 10^5$ M^{-1} s^{-1}.

Besides the desired lifetime τ_A, the analysis via eq 10 yielded the lifetimes τ_2 and τ_B. τ_2 was always in the diffusion-controlled regime. For the solutions containing cyclohexane and cyclopentane, the lifetimes τ_B of the methyl radical were as found for the substrate free solutions; that is, the reaction of methyl with the substrates is slow. For the anisole-containing solutions, the lifetime τ_B of the anisyl radical was about 10−15 ms and not interpreted. The radical resulting from *tert*-butylbenzene rearranges, and its τ_B is treated in detail below.

The rate constants measured in this work for the β-scission and hydrogen abstractions not only confirm earlier views[10,11] but also extend the knowledge of *tert*-butoxyl radical kinetics. They allow the conversion of many additional relative rate data[1c] to the absolute scale.

Other Radical Rearrangements and Fragmentations

The reactions considered in this section have been kinetically studied before to different degrees of precision. We reinvestigate them here to provide additional absolute rate data and to confirm that the analysis of the concentrations of both the rearranging and the rearranged species yields the same information.

Neophyl Rearrangement. The primary alkyl radical (neophyl) formed by the hydrogen abstraction from a methyl group of *tert*-butylbenzene (vide supra) undergoes a 1,2-phenyl shift to the 2-benzylprop-2-yl radical.[1] Steady-state ESR spectra taken during photolysis of 20 vol % di-*tert*-butyl peroxide in *tert*-butylbenzene at 258 K show strong features of neophyl and very little contamination by methyl radicals stemming from β-scission. In fact, the rate constant of the β-scission is estimated as $k_{\beta,258} = 870$ s^{-1} (from the activation parameters for the solvent benzene) and is much smaller than the pseudo-first-

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(20) (a) Schwetlick, K.; Karl, R.; Jentzsch, J. *J. Prakt. Chem.* **1963**, *22*, 113–124. (b) Sakurai, H.; Hosomi, A.; Kumada, M. *J. Org. Chem.* **1970**, *35*, 993–996.
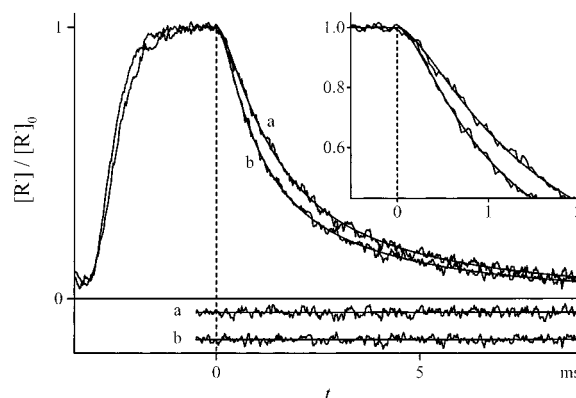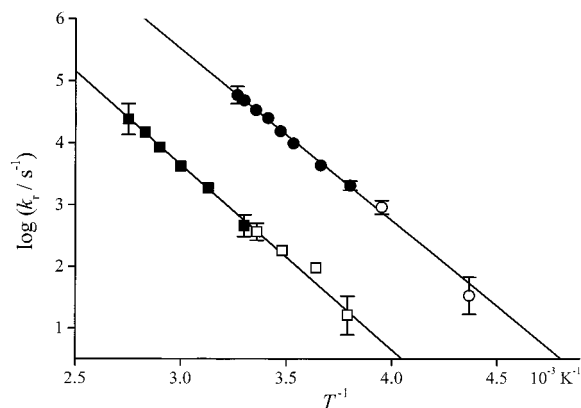
Figure 5. 2-Benzylprop-2-yl concentrations vs time at (a) 319 ± 1 K and (b) 333 ± 1 K and fits of eq 10 to the data. Bottom traces are residuals of fits, and the inset shows an expansion of the traces around $t = 0$ s.

order rate constant for the hydrogen abstraction of about 3.8×10^4 s^{-1} (from the activation parameters and a substrate concentration of 5 M). At higher temperatures the neophyl radical is increasingly replaced by the rearranged species. Methyl stays minor, and there is an additional weak quartet belonging to an unidentified radical. In the analysis these contaminations were neglected.

At lower temperatures of 264−298 K, the rate constants of the rearrangement k_r were determined from the time-dependent concentration of the neophyl radical. To allow for the noninstant hydrogen abstraction ($k_{H,280}$[*tert*-butylbenzene] = 1 × 10⁵ s^{-1}), we used eq 10 for temperatures between 264 and 275 K, and k_r was obtained as τ_B^{-1}. For 287−298 K the neophyl formation is practically instantaneous on the observation time scale, so that eq 9 was fitted to the data ($k_r = \tau_A^{-1}$). For still higher temperatures of 303−363 K, the concentration of the rearranged radical was followed, and the analysis used eq 10 with $k_r = \tau_A^{-1}$. Figure 5 shows two kinetic traces obtained for the rearranged radical in the high-temperature range together with fits to eq 10. At the onset of the dark period the delayed formation is again clearly visible.

The lifetime τ_B of the rearranged species was large ($\tau_B > 15$ ms); that is, it is kinetically insignificant, and the second-order lifetime was about 900 μs. Measurements at various temperatures of the concentrations of both the rearranging and the rearranged radical lead to the data shown in Figure 6, to $k_{r,298} = 402$ s^{-1}, and to the activation parameters

$$\log(k_r/s^{-1}) = (12.7 \pm 0.3) - (57.6 \pm 1.5)/2.303RT \quad (16)$$

Absolute Rate Constants for the tert-Butoxyl Radical

J. Am. Chem. Soc., Vol. 121, No. 32, 1999 7387

Figure 6. Rate constants and fits to the Arrhenius equation for the neophyl (squares) and of the 2-methyloxiran-2-yl (circles) rearrangements: open symbols, observation of the rearranging radical; closed symbols, observation of the rearranged radical.

where the activation energy is again given in kJ/mol and the errors are standard deviations.

In early work, we estimated an activation energy in the temperature range from 290 to 340 K of $E_a = (43 \pm 9)$ kJ/mol.[21a] Ingold et al.[21b] combined steady-state concentrations with directly determined second-order lifetimes and obtained the more exact relation $\log(k_r/s^{-1}) = (11.7 \pm 1.0) - (56.8 \pm 4.2)/2.303RT$ for 283−307 K. From product yields, Franz et al.[21c] deduced k_r relative to the trapping of the neophyl radical by tri-*n*-butylstannane. With the known temperature dependence of the latter reaction, they arrived at $\log(k_r/s^{-1}) = (11.6 \pm 0.3) - (45.5 \pm 2.0)/2.303RT$ for 393−492 K, and this relation was accepted by Ingold et al.[21d] When more exact data for the reaction of alkyl radicals with the stannane became available, these results were corrected to $\log(k_r/s^{-1}) = 11.0-45.3/2.303RT$.[21e] Our activation parameters agree best with the earlier results of Ingold et al.[21b] and hold for a large temperature range. In comparison to the more recent other determinations,[21c,e] both our frequency factor and our activation energy are higher, and the frequency factor appears even too high in view of earlier discussions.[21c] However, it should be noted that, because of error compensation effects, the different Arrhenius parameters yield rather similar rate constants, for example, at 343 K $k_r = 12.5 \times 10^4$ s^{-1} from the latest literature data[21e] vs $k_r = 8.5 \times 10^4$ s^{-1} from eq 16, their difference being within the error limits.

Ring Opening of the 2-Methyloxiran-2-yl Radical. Di-*tert*-butyl peroxide (20 vol %) photolyzed in (±)-2-methyloxirane yields the 2-methyloxiran-2-yl radical as the major and the 2-methyloxiran-3-yl radical as the minor species,[22a,b] in accord with quantum chemical calculations of the radical stabilities.[22c] The former radical undergoes a facile ring opening to the acetonyl radical. Steady-state ESR spectra taken during the reactions agreed with those given earlier.[22a,b] Under neglect of the minor species, the rate constants of the ring opening were determined for low temperatures (229−253 K) from the time-dependent concentration of 2-methyloxiran-2-yl via eq 9 ($k_r = \tau_A^{-1}$). The formation of this radical is practically instantaneous.
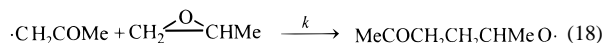
(21) (a) Hamilton, E. J., Jr.; Fischer, H. *Helv. Chim. Acta* **1973**, *56*, 795−799. (b) Maillard, B.; Ingold, K. U. *J. Am. Chem. Soc.* **1976**, *98*, 1224−1226. (c) Franz, J. A.; Barrows, R. D.; Camaioni, D. M. *J. Am. Chem. Soc.* **1984**, *106*, 3964−3967. (d) Lindsay, D. A.; Lusztyk, J.; Ingold, K. U. *J. Am. Chem. Soc.* **1984**, *106*, 7078−7090. (e) Burton, A.; Ingold, K. U.; Walton, J. C. *J. Org. Chem.* **1996**, *61*, 778−3782.

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This is indicated also by the absence of methyl in steady-state spectra and is in accord with the high rate constant $k_{273} = 5.2 \times 10^5$ M^{-1} s^{-1} for the hydrogen abstraction which follows from our average activation parameters for cyclohexane (Table 2) and relative abstraction rate constants measured by Walling et al.[22d] For higher temperatures (263−306 K), the concentration of the acetonyl radical was analyzed with eq 10 ($k_r = \tau_A^{-1}$). The results from both radicals are displayed in Figure 6, lead to $k_{r,298} = 3.1 \times 10^4$ s^{-1} and are expressed by

$$\log(k_r/s^{-1}) = (13.8 \pm 0.3) - (53.1 \pm 1.3)/2.303RT \quad (17)$$

Our earlier estimate from steady-state radical concentrations was $\log(k_r/s^{-1}) = (15 \pm 1) - (62.7 \pm 8.4)/2.303RT$,[22b] but the frequency factor is too high. Other data seem not available. The decay of acetonyl showed an appreciable first- or pseudo-first-order decay component τ_B. This may be due to the reaction with the methyloxirane solvent, which was inferred by Wallace et al.[23] to explain the formation of 5-hydroxy-2-hexanone in the reaction system

$$\cdot CH_2COMe + CH_2 \overset{O}{\diagup}\!\!\diagdown CHMe \xrightarrow{k} MeCOCH_2CH_2CHMe\,O\cdot \quad (18)$$

The temperature dependence of $\tau_B^{-1} = k[\text{2-methyloxirane}]$ leads to $\log(k/\text{M}^{-1}\text{ s}^{-1}) = (5.4 \pm 0.8) - (25.2 \pm 2.1)/2.303RT$ for this reaction, but the low-frequency factor sheds doubt on the interpretation.

Decarboxylation of the *tert*-Butoxycarbonyl Radical. Photolysis of 20 vol % di-*tert*-butyl peroxide in *n*-heptane containing 1.0 M *tert*-butyl formate generates *tert*-butoxycarbonyl radicals[2a,18e,24] by hydrogen abstraction of *tert*-butoxyl radicals from the substrate. For ethyl formate an absolute rate constant for the hydrogen abstraction $k = 5.1 \times 10^5$ M^{-1} s^{-1} at 297 K is available,[24b] and the high value ensures again instant formation of the alkoxycarbonyl species. Decarboxylation of *tert*-butoxycarbonyl gives *tert*-butyl, and both radicals can be monitored by ESR spectroscopy.[2a,18e] The rate constants of the decarboxylation were determined at low temperatures (219−244 K) from the time-dependent concentration of the *tert*-butoxycarbonyl radical analyzed with eq 9 and for higher temperatures (242−302 K) from the signal profile of *tert*-butyl analyzed with eq 10. They are shown in Figure 7, give $k_{r,298} = 8.1 \times 10^4$ s^{-1}, and follow the relation

$$\log(k_r/s^{-1}) = (13.6 \pm 0.2) - (49.6 \pm 0.7)/2.303RT \quad (19)$$

In our earlier work[2a] the *tert*-butoxycarbonyl radicals were produced by photolysis of *tert*-butylpivalate in the range 225 K < T < 253 K, and the rate constants were determined by a simultaneous multiparameter fit of numerically integrated rate equations to the traces of both radicals. This avoided the assumption of equal termination constants, which were found to differ by a factor of 2. The decarboxylation obeyed $\log(k_r/s^{-1}) = (13.8 \pm 0.2) - (49.0 \pm 1.2)/2.303RT$, in perfect agreement with the present results which confirms the validity of the new much simpler analysis. Good agreement is also observed with the results of Roberts et al. obtained by laser flash electron spin resonance under kinetic isolation conditions as $\log(k_r/s^{-1}) = (13.2 \pm 0.3) - (45.2 \pm 1.5)/2.303RT$.[18e]

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(24) (a) Griller, D.; Roberts, B. P. *J. Chem. Soc., Perkin Trans. 2* **1972**, 747−751. (b) Chatgigliaglu, C.; Lunazzi, L.; Macciantelli, D.; Placucci, G. *J. Am. Chem. Soc.* **1984**, *106*, 5252−5256.
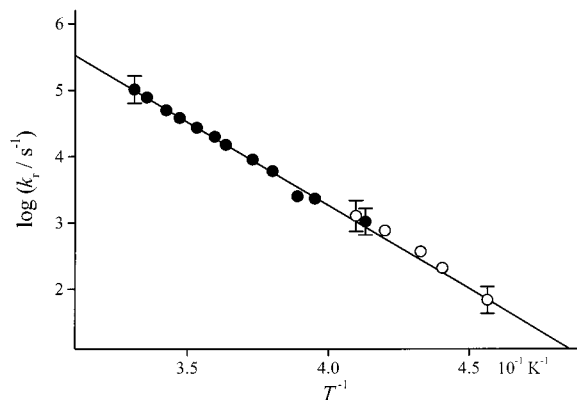
Figure 7. Rate constants and fits to the Arrhenius equation for the decarboxylation of the *tert*-butoxycarbonyl in *n*-heptane: open symbols, observation of the rearranging radical; closed symbols, observation of the rearranged radical.

In summary, in this work we have extended the analysis of the time dependence of radical concentrations observed during intermittent photochemical radical generation and during competing reactions to delayed radical formations in the off-period of generation. The technique was applied to obtain absolute rate constants and their activation parameters for a variety of reactions and has proven its versatility. Measurable first- or pseudo-first-order lifetimes range from 10 μs to about 10 ms, which means that rate constants of 10^2-10^5 s^{-1} for first-order processes or $10-10^8$ M^{-1} s^{-1} for pseudo-first-order reactions are accessible. The requirement of similar termination constants for different radicals involved in the competing reactions is expected to be fulfilled in most realistic cases.

Supporting Information Available: Two tables with results of fits to numerically integrated kinetic equations, five figures with ESR spectra, two figures on the importance of the sector error, and one figure showing the temperature dependence of the hydrogen abstractions from *tert*-butylbenzene and anisole. This material is available free of charge via the Internet at http://pubs.acs.org.

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