Absolute Rate Constants for the Addition of the 1-(*tert*-Butoxy)carbonylethyl Radical to Alkenes in Solution

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Absolute rate constants and some of their *Arrhenius* parameters are reported for the addition of the 1-[(*tert*-butoxy)carbonyl]ethyl radical ($Me\dot{C}HCO_2Me_3$) to several mono- or 1,1-disubstituted alkenes in acetonitrile as obtained by time-resolved electron spin resonance spectroscopy. At 295 K, the rate constants range from 470 $M^{-1} s^{-1}$ (but-1-ene) to $2.4 \cdot 10^5$ $M^{-1} s^{-1}$ (1,1-diphenylethene), the experimental activation energies range from 26.8 kJ/mol (but-1-ene) to 14.7 kJ/mol (styrene), and the frequency factors obey on the average $\log (A/M^{-1} s^{-1}) = 7.9 \pm 0.5$. The rate constants of the secondary 1-[(*tert*-butoxy)carbonyl]ethyl radical are close to the geometric mean of those of the related primary [(*tert*-butoxy)carbonyl]methyl and the tertiary 2-(methoxycarbonyl)propan-2-yl radicals. The activation energies for addition of these three carboxy-substituted alkyl radicals are mainly governed by the addition enthalpy but are also substantially lowered by ambiphilic polar effects. The results support a previously derived predictive analysis, and relations to rate constants of acrylate polymerizations are discussed.

1. Introduction. – The addition of C-centered radicals to C=C bonds has many applications in organic and polymer chemistry [1]. With radical and substrate substitution, the rate constants vary by many orders of magnitude and reflect an interplay of polar, steric, and enthalpic effects. To quantify these effects, we have measured the rate constants and their temperature dependence for the addition of a large variety of C-centered radicals to many alkenes in liquid solution by time-resolved electron spin resonance (ESR) and other techniques [2]. A recent comprehensive analysis of all available data for additions to mono- and 1,1-disubstituted alkenes [3] has revealed that the frequency factors of additions of primary, secondary, and tertiary C-centered radicals fall into distinct and narrow ranges. Therefore, the huge rate variations are mainly due to changes of the activation energies with alkene and radical substitution. These decrease generally with increasing exothermicity of the addition, but they are often also strongly diminished by polar substituent effects. An equation was found which allowed the rationalization and the prediction of rate constants within one order of magnitude or better.

So far, the series included the primary and the tertiary ester substituted radicals [(*tert*-butoxy)carbonyl]methyl ($\dot{C}H_2CO_2CMe_3$, MEst) [2j] and 2-(methoxycarbonyl)-propan-2-yl ($Me_2\dot{C}CO_2CH_3$, PEst) [2s]. It is extended here to the corresponding secondary 1-[(*tert*-butoxy)carbonyl]ethyl radical ($Me\dot{C}HCO_2CMe_3$, EEst) for several reasons: first, it is of interest to compare the reactivity of primary, secondary, and tertiary radicals that differ only by Me substitution. Then, the value suggested earlier for the average frequency factor of additions of secondary radicals to mono- and 1,1-disubstituted alkenes [3] needs further support. Moreover, additional rate constants and activation energies are clearly necessary to test our predictive equation. Finally, EEst is electronically similar to the propagating radical of acrylates, so that the factors controlling its addition are expected to hold as well in acrylate polymerizations. Acetonitrile (MeCN) was chosen as solvent because it is relatively inert to radical attack, and solvent effects on the rate constants should be of minor importance [2g].

2. Results and Discussion. – The 1-[(*tert*-butoxy)carbonyl]ethyl radical EEst was generated by the *Norrish* type-I (*Eqn. 1*) photocleavage of the corresponding disubstituted ketone 2,4-dimethyl-3-oxoglutaric acid di(*tert*-butyl) ester ($(Me_3CO\text{-}OCCHMe)_2CO$) 30 mM in MeCN solution. The decarbonylation (*Eqn. 2*) of the acyl radical is so fast that this radical was not detected at −50° and above. Besides the expected species EEst ($Me\dot{C}HCO_2CMe_3$, $g = 2.0033 \pm 0.0001$, $a(H_\alpha) = (20.53 \pm 0.04)$ G, $a(3\,H_\beta) = (24.44 \pm 0.05)$ G at 297 K), a weak signal of PEst ($Me_2\dot{C}CO_2CMe_3$, $g = 2.0033 \pm 0.001$, $a(6\,H_\beta) = (21.5 \pm 0.1)$ G at 297 K), was also detected. It arises from the side product of the synthesis and contributed less than 6% to the total spectrum (*Fig. 1*, inset).

$$(Me_3CO_2CCHMe)_2CO \xrightarrow{h\nu} \dot{C}OCHMeCO_2CMe_3 + CH_3\dot{C}HCO_2CMe_2 \qquad (1)$$

$$\dot{C}OCHMeCO_2CMe_3 \longrightarrow Me\dot{C}HCO_2CMe_3 + CO \qquad (2)$$

Solutions containing alkenes showed ESR spectra of radicals formed by addition of EEst to the alkene CH_2 groups. The magnetic properties for the adducts to acrylonitrile

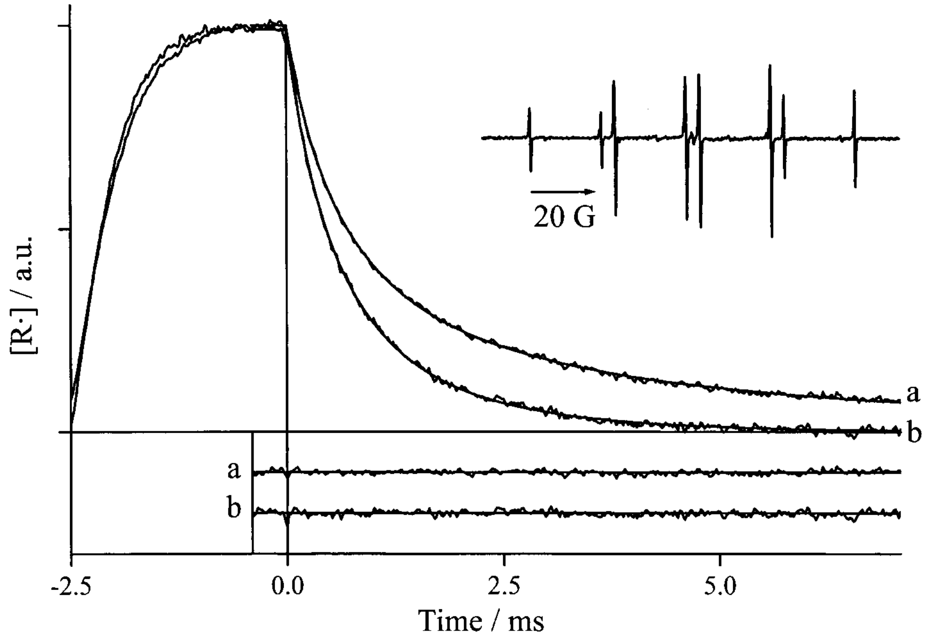

Fig. 1. *Concentration of the 1-[(*tert*-butoxy)carbonyl]ethyl radical (EEst)* vs. *time* a) *in the absence of alkene and* b) *in the presence of 7 mM methacrylonitrile.* Bottom traces are residuals of the fits. The inset shows a steady-state ESR spectrum.

($g = 2.0032$, $a(\text{H}_\alpha) = 20.3$ G, $a(2\,\text{H}_\beta) = 23.3$ G, $a(1\text{N}_\beta) = 3.4$ G), trimethyl(vinyl)silane ($g = 2.0025$, $a(\text{H}_\alpha) = 20.1$ G, $a(2\,\text{H}_\beta) = 24.4$ G), and *tert*-butyl acrylate ($g = 2.0028$, $a(\text{H}_\alpha) = 20.4$ G, $a(2\,\text{H}_\beta) = 22.1$ G, $a(\text{H}_\gamma) = 0.9$ G) are in usual ranges [4]. Obviously, the addition occurs predominantly at the unsubstituted C-atom of the alkenes, as it has been found previously for many C-centered radicals [1–3].

Kinetic traces of EEst obtained under intermittent photolysis at 295 K in alkene-free solutions (*Fig. 1*, trace *a*) show a second-order decay ($\tau_2 \approx 740$ µs) that is slightly perturbed by a first or pseudo-first-order process ($\tau_{10} = 30$ ms). The latter is attributed to reactions with the starting compounds and/or products. The self-termination constant of EEst was determined as $2k_\text{t}(\text{EEst}) = (4.1 \pm 0.3) \cdot 10^9 \text{M}^{-1}\text{s}^{-1}$ and is close to the diffusion-controlled limit. When alkenes are present (*Fig. 1*, trace *b*), the kinetics reveal a larger pseudo-first-order contribution that depends on the alkene concentration. Trace *b* in *Fig. 1* corresponds to 7 mM methacrylonitrile and is characterized by a shorter $\tau_1 = 2.1$ ms ($\tau_2 = 780$ µs). The lifetimes $\tau_1 = (k[\text{A}])^{-1}$ were obtained for different alkene concentrations [A]. Plots of τ^{-1} *vs.* [A] were linear and provided the rate constants *k* from the slopes [2]. The activation parameters were obtained by fits of the *Arrhenius* expression to data measured at various temperatures.

All results are collected in the *Table* in which the alkenes are ordered according to increasing addition rate constant of the methyl radical. EEst closely follows that ordering. Also given are the ranges of alkene concentrations, the number of experiments evaluated for the determination of the rate constants, and the *Arrhenius* parameters for several alkenes.

Table. *Absolute Rate Constants* k *at (295 ± 1) K*, *Frequency Factors* A, *Experimental and Calculated Activation Energies* E_a *and* E_a^{cal} (average frequency factor log (A) = 7.9) *for the Addition of the 1-(*tert-*Butoxy)carbonylethyl Radical to Alkenes ($CH_2{=}CXY$) in MeCN.* Standard deviations in brackets, ranges of alkene concentrations *c* at 295 K and numbers *n* of evaluated kinetic experiments.

X	Y	*c* [mM]	*n*	*k* [$\text{M}^{-1}\text{s}^{-1}$]	E_a [kJ/mol]	log (A/$\text{M}^{-1}\text{s}^{-1}$)	E_a^cal [kJ/mol]
H	Et	20–590	68	470(20)	26.8(32)	7.4(5)[a]	29.6
Me	Me	74–330	20	880(80)			28.1
Me	MeO	130–440	12	1430(30)			26.9
Me	AcO	20–80	58	1100(20)	26.8(12)	7.8(2)[b]	27.6
H	EtO	47–170	12	1800(150)			26.3
H	AcO	60–250	12	1450(100)			26.9
H	Cl	110–460	60	1500(700)	22.9(20)	7.3(4)[b]	26.8
H	Me_3Si	5–40	55	1600(300)	27.5(25)	8.1(4)[b]	26.6
Me	Cl	22–220	16	4300(200)			24.2
Cl	Cl	5–20	60	11000(2000)	24.1(31)	8.5(5)[b]	21.9
H	CO_2Me	7.5–30	71	15000(3700)	19.1(35)	7.7(6)[c]	21.1
Me	CO_2Me	1.5–7.4	13	60000(3400)			17.9
H	CN	1.8–7.3	60	40000(3400)	22.0(28)	8.5(5)[b]	18.8
H	CHO	2.7–10.3	12	44000(7000)			18.5
Me	CN	1.5–7	12	68000(5000)			17.4
H	Ph	0.5–5.4	48	93000(8000)	14.7(12)	7.6(2)[b]	16.7
Me	Ph	0.7–3.1	12	129000(10000)			15.9
Ph	Ph	0.52–1.70	12	240000(10000)			14.3

[a]) 295–323 K. [b]) 273–323 K. [c]) 274–314 K.

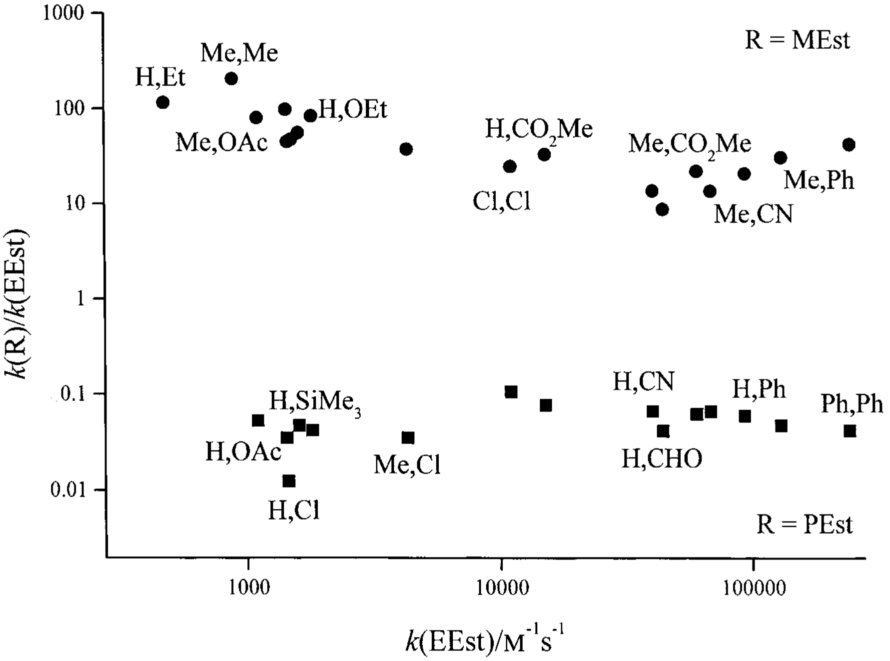

Fig. 2. *Rate constants for the additions of the radicals [(*tert*-butoxy)carbonyl]methyl (MEst) and 2-(methoxycarbonyl)propan-2-yl (PEst) in relation to the rate constants of 1-[(*tert*-butoxy)carbonyl]ethyl (EEst)*

Comparison of MEst, EEst, and *PEst.* To compare the reactivity of the three ester-substituted radicals, we show in *Fig. 2* the ratios of the rate constants k(MEst)/k(EEst) and k(PEst)/k(EEst) at room temperature plotted *vs.* k(EEst). The individual rate constants of all three radicals vary by a factor of nearly 500, but the trends with alkene substitution are very similar. Thus, the tertiary radical PEst reacts between 10 and 83 times and on the average 19 times slower than EEst. On the other hand, EEst reacts between 9 to 200 times and on the average 54 times slower than the primary MEst. A closer inspection reveals that the ratio k(MEst)/k(EEst) is above average for alkenes with electron-donor substituents (H,Et; Me,Me; H,EtO). Hence, MEst is more electrophilic than EEst and PEst, as it is expected from the missing Me substituents. Nevertheless, the close resemblance of the reactivities suggests that the rate constants of EEst, MEst, and PEst are governed by very similar factors and are interrelated.

One may speculate that the activation entropies and enthalpies of MEst and PEst can be averaged linearly to provide those of EEst. Hence, the geometric mean $(k(\mathrm{MEst}) \cdot k(\mathrm{PEst}))^{1/2}$ should approximate k(EEst). In fact, this mean correlates linearly with k(EEst) with a slope of 0.92 and $R^2 = 0.96$, and the average of the decadic logarithms $(\log(k(\mathrm{MEst})) + \log(k(\mathrm{PEst})))/2$ approximates $\log(k(\mathrm{EEst}))$ for all alkene with an offset of -0.095 and a standard deviation of 0.15, that is within 40% of the measured values. It is expected that such a geometric-mean rule can be applied quite generally to estimate the addition rates of secondary radicals from those of the corresponding primary and tertiary species.

Frequency Factors. The frequency factors given in the *Table* are in the narrow range of $7.3 < \log(A/\mathrm{M}^{-1}\mathrm{s}^{-1}) < 8.5$. A comparison with those of other C-centered radicals [2][3] shows no specific dependence on the alkene substituents. Therefore, we assume that the variation is not significant, but that it is caused by the well-known error compensation of the *Arrhenius* parameters [5]. The average logarithm of all frequency factors of EEst is $\log(A/\mathrm{M}^{-1}\mathrm{s}^{-1}) = 7.9 \pm 0.5$. This agrees very well with the previously suggested average for secondary radicals of $\log(A/\mathrm{M}^{-1}\mathrm{s}^{-1}) = 8$ [3], which was found for a malonyl-type radical [2r]. For primary radicals like MEst, the average frequency factor is $\log(A/\mathrm{M}^{-1}\mathrm{s}^{-1}) = 8.5$ and for tertiary radicals like PEst, it is $\log(A/\mathrm{M}^{-1}\mathrm{s}^{-1}) = 7.5$ [3]. Undoubtedly, the decrease of the frequency factor from the primary to the secondary and from the secondary to tertiary Me-substituted species is due to the increasing hindrance of the Me-group rotations in the transition state. If the activation energies were equal, the ratios of the rate constants MEst/EEst and EEst/PEst should amount to 3. The experimental ratios are considerably larger (*Fig. 2*), and this means that the activation energies increase in the order MEst < EEst < PEst.

Activation Energies. To extend the set of available activation energies for EEst, they were recalculated for all alkenes from the rate constants with the average frequency factor $\log(A/\mathrm{M}^{-1}\mathrm{s}^{-1}) = 7.9$ and are also displayed in the *Table*. In the discussion of these data, we now follow closely the earlier analysis of activation barriers in terms of the *State Correlation Diagram*, which was developed by *Shaik et al.* for the general interpretation of chemical reactivities [6] and specified later for radical additions [3].

In principle, the energy and the location of the transition state should depend on the exothermicity H_r of the addition. We have shown [3] that this can be expressed by an *Evans-Polanyi-Semenov*-type equation [7] for the activation energy (*Eqn. 3*)

$$E_{\mathrm{a,EPS}}/\mathrm{kJ\ mol^{-1}} = 50 + 0.22\ H_r/\mathrm{kJ\ mol^{-1}}. \tag{3}$$

The observed energies are often smaller than those predicted from *Eqn. 3* because of additional polar effects. These reflect the mixing of charge-transfer configurations like R^+A^- and R^-A^+ with the ground-state configuration RA, which lowers the barrier. Here, R and A denote the radical and the alkene, respectively. The polar contributions increase with decreasing energy gaps $IE(\mathrm{R}) - EA(\mathrm{A})$ and $IE(\mathrm{A}) - EA(\mathrm{R})$ between R^+A^- and R^-A^+ and RA, where IE is the ionization energy and EA the electron affinity. Further, they increase with increasing *Coulomb* attraction C between the ions in the transition state and with an increasing interaction parameter γ. Systems with considerable charge and spin delocalization such as radicals and alkenes with Ph substituents have relatively small parameters C and γ and exhibit less polar effects.

To cover the polar effects we suggested the general equation for the activation energy

$$E_a/\mathrm{kJ\ mol^{-1}} = (50 + 0.22\ H_r/\mathrm{kJ\ mol^{-1}})F_n F_e, \tag{4}$$

where the polar factors $0 < F_n, F_e < 1$ are given by the functions

$$F_n = 1 - \exp[-((IE(\mathrm{R}) - EA(\mathrm{A}) - C_n)/\gamma_n)^2], \tag{5}$$

$$F_e = 1 - \exp[-((IE(\mathrm{A}) - EA(\mathrm{R}) - C_e)/\gamma_e)^2]. \tag{6}$$

In principle, the parameters $C_{n,e}$ and $\gamma_{n,e}$ may vary from system to system. However, the earlier analysis of many activation energies showed that they vary only in rather narrow ranges, and *Eqns. 4–6* were found to accommodate the available data very well. The activation energies for EEst now allow a further test of these equations. This, however, requires to specify the entering quantities first.

The addition enthalpies H_r are not known for EEst but can be estimated from bond dissociation energies *BDE* and molar heats of formation h_f by a thermochemical procedure developed before [2][3]. We consider the overall reaction

$$\mathrm{RH} + \mathrm{A} \rightarrow \dot{\mathrm{R}} + \dot{\mathrm{H}} + \mathrm{A} \rightarrow \dot{\mathrm{H}} + \mathrm{R}\dot{\mathrm{A}} \rightarrow \mathrm{RAH} \tag{7}$$

from which the enthalpy for the addition step is at 298°K

$$H_r(\dot{\mathrm{R}}) = h_f(\mathrm{RAH}) - h_f(\mathrm{RH}) - h_f(\mathrm{A}) + BDE(\mathrm{RA{-}H}) - BDE(\mathrm{R{-}H}) \tag{8}$$

From previous work [2p][3], H_r is known for the addition of the methyl radical (Me) to many alkenes. Therefore, we use these data and increment for the replacement of Me by EEst *via Eqn. 9*

$$\begin{aligned} H_r(\mathrm{EEst}) = H_r(\mathrm{Me}) + h_f(\mathrm{EEstAH}) - h_f(\mathrm{MeAH}) - h_f(\mathrm{EEstH}) + h_f(\mathrm{CH_4}) \\ + BDE(\mathrm{Me{-}H}) - BDE(\mathrm{EEst{-}H}) \end{aligned} \tag{9}$$

Further, we use ethene as substrate A because the required energies are available for this alkene, and we use the increment for ethene also for all other compounds.

Experimentally known are the (gas phase) standard heats of formation $h_f(\mathrm{CH_4}) = -74.5$ kJ/mol [8], $h_f(\mathrm{MeAH}) = h_f(\mathrm{MeCH_2Me}) = -104.5$ kJ/mol [9] and $BDE(\mathrm{Me{-}H}) = 439$ kJ/mol [10]. The remaining energies were kindly calculated for this work by *Scott* and *Radom* [11] for the methyl ester as $h_f(\mathrm{EEstH}) = -433.3$ kJ/mol, $h_f(\mathrm{EEstAH}) = -479.3$ kJ/mol and $BDE(\mathrm{EEst{-}H}) = 385.5$ kJ/mol by the quantum-chemical G3(MP2)/B3-LYP method. The reliability of the calculation is confirmed by the good agreement of $h_f(\mathrm{EEstH})$ with an experimental value of -432 kJ/mol [8]. With these data, *Eqn. 9* renders the addition of EEst to ethene by 37 kJ/mol less exothermic than that of the Me. Combination of this increment with the known enthalpies of the additions of the Me to all alkenes of the *Table* [2p][3] yields values for H_r ranging from -57 kJ/mol (substituents Me, OMe) to -116 kJ/mol (Ph, Ph).

Of course, the estimations may produce considerable errors of H_r up to *ca.* 15 kJ/mol in unfavourable cases [2p][3]. However, these errors are smaller than the absolute values, and they are transmitted to the activation energies *via Eqn. 4* by 22% only.

In comparison, the addition of EEst is by *ca.* 11 kJ/mol less exothermic than that of MEst [3]. This is mainly due to the increased radical stabilization by the Me group. On the other hand, EEst has also a 5 kJ/mol lower reaction enthalpy than PEst [3]. The latter difference is contrary to chemical intuition. However, it is rather small and may be due to an inaccurate estimation of H_r for PEst [2s]. In fact, for A = ethene the difference of the heats of formation $|h_f(\mathrm{RAH}) - h_f(\mathrm{RH})| = 55$ kJ/mol [2s] is suspiciously larger for R = PEst than for R = MEst (42.5 kJ/mol) and R = EEst (46 kJ/mol).

In *Fig. 3*, the activation energies for the additions of EEst are plotted against the estimated reaction enthalpies. They follow the relation $E_a/\mathrm{kJ\ mol^{-1}} = (41 \pm 2) +$

(0.24 ± 0.03) H_r/kJ mol^{-1} with a correlation coefficient $R^2 = 0.82$. All experimental activation energies are by *ca.* 8 to 14 kJ/mol lower than expected from *Eqn. 3* for additions without accounting for polar effects (broken line in *Fig. 3*). The same behavior was also observed for MEst and PEst [3]. It is typical for ambiphilic radicals for which the addition to electron-deficient alkenes is accelerated by nucleophilic and that to electron-rich alkenes by electrophilic polar effects [3], and it has been formulated previously that mono-carboxy substituted radicals belong to that class [12].

In general, polar effects become important when the energy gaps between the charge transfer and the ground-state configurations $IE(\mathrm{R}) - EA(\mathrm{A})$ and $IE(\mathrm{A}) - EA(\mathrm{R})$ fall below 8–9 eV. For EEst, the (gas-phase) vertical ionization energy is $IE(\mathrm{EEst}) = 8.19$ eV, and the electron affinity is $EA(\mathrm{EEst}) = 1.44$ eV [11]. Combination of these values with the ionization energies and the electron affinities of the alkenes [3] shows that the addition of EEst should exhibit appreciable electrophilic polar effects towards all alkenes of the *Table* with the exception of the very electron-deficient acrylonitrile and methacrylonitrile. On the other hand, strong nucleophilic polar rate enhancements are expected only for the carboxy-, carbonyl-, and cyano-substituted compounds.

The earlier analysis of the activation energies [3] has provided values for the parameters of *Eqns. 4–6* C and γ, as $C_n = 6.0$ eV, $C_e = 4.5$ eV, $\gamma_n = (1.5-3.2)$ eV, and

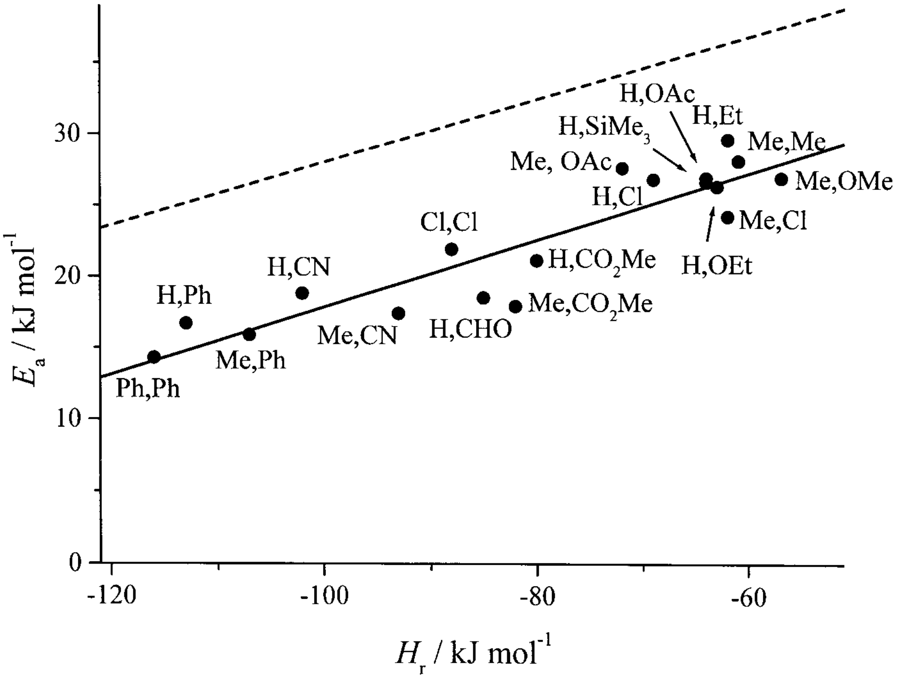

Fig. 3. *Activation energies* E_a *for the addition of the 1-[(*tert*-butoxy)carbonyl]ethyl radical (EEst) to alkenes as a function of the reaction enthalpy* H_r. The solid line corresponds to E_a/kJ mol^{-1} = (41 ± 2) + (0.24 ± 0.03) H_r/kJ mol^{-1}, $R^2 = 0.82$) and the dashed line to the behavior expected without polar effects (E_a/kJ mol^{-1} = 50 + 0.22 H_r/kJ mol^{-1}).

$\gamma_e = (3.0-4.3)$ eV for radicals and alkenes without Ph substituents, and $C_n = 5.5$ eV, $C_e = 4.0$ eV, $\gamma_n = (0.75-3.2)$, and $\gamma_e = (2.5-4.0)$ eV for radicals and alkenes with Ph substituents. Grossly, the interaction parameters γ increase with increasing charge and spin localization in the transition state.

Since MEst and PEst bracket the reactivity of EEst, it is tempting to try the average of their parameters for EEst also, that is $C_n = 6.0$ eV, $C_e = 4.5$ eV, $\gamma_n = 2.25$ eV and $\gamma_e = 2.5$ eV for alkenes without Ph substituents, and $C_n = 5.5$ eV, $C_e = 4.0$ eV, $\gamma_n = 1.13$, and $\gamma_e = 2.5$ eV for alkenes with Ph substituents. In fact, this already provides a reasonable description of the activation energies of the EEst additions. However, an even better agreement between calculated and observed activation energies is found when slightly higher values are used for γ_n, namely $\gamma_n = 2.4$ eV for alkenes without Ph substituents and $\gamma_n = 1.5$ eV for alkenes with Ph substituents.

Fig. 4 shows the activation energies calculated with these parameters and *Eqns. 4–6* *vs.* the experimental data. The solid line represents the equality of calculation and experiment, and the individual points scatter around this line with a standard deviation of 1.95 kJ/mol and a maximum excursion of *ca.* 5 kJ/mol. Hence, the new rate data for the addition of EEst to alkenes nicely confirm the predictive power of our earlier *State Correlation Diagram* analysis [3] although the empirical parameters *C* and γ still need theoretical justifications.

Relations to Acrylate Polymerizations. The radical EEst ($\mathrm{Me\dot{C}HCO_2CMe_3}$) is structurally similar to the propagating radicals of acrylates ($\mathrm{R-CH_2\dot{C}HCO_2R'}$, R = polymer chain, R′ = alkyl group). For the larger propagating radical, one expects a

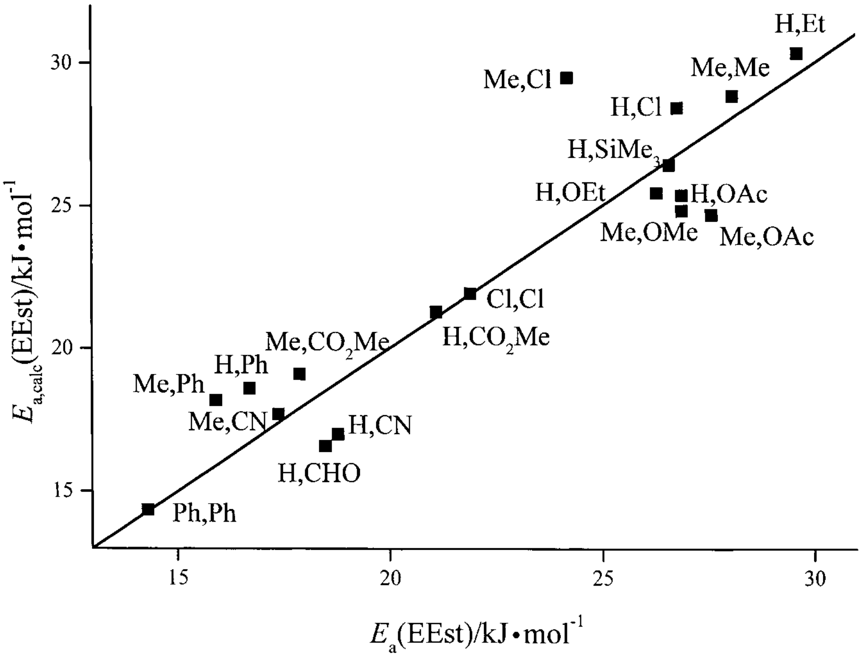

Fig. 4. *Calculated* vs. *experimental activation energies.* The solid line corresponds to the equality.

smaller frequency factor [3] so that its addition rate constants should be smaller than those of EEst. At 295 K, the addition rate constant of EEst to methyl acrylate is $k = 15000\ \text{M}^{-1}\text{s}^{-1}$ (*Table*). It is astonishing that the homopropagation constant of methyl acrylate is practically identical with $k_p = 15000\text{M}^{-1}\text{s}^{-1}$ [13]. However, we have recently determined the addition rate constants of the radicals $R{-}CH_2\dot{C}HCO_2Me$ with R = CH_2OH, Ph, $MeCH(OH)CH_2$, and *t*-Bu to methyl acrylate as $k = 18100$, 22400, 3300, and $6100\ \text{M}^{-1}\text{s}^{-1}$, respectively, at 295 K [3][14]. This shows that the rate constants are influenced by the residue R, and each case deserves an individual discussion.

In general, the general reactivity patterns of EEst and of the acrylate propagation radical are very similar. This is seen in *Fig. 5* where the ratio of the rate constants $r_1^{\text{cal}} = k(\text{EEst, methyl acrylate})/k(\text{EEst, alkene})$ is plotted *vs.* the copolymerization parameters of methyl acrylate $r_1^{\text{exp}} = k_p/k(\text{alkene})$ [15]. The solid line is $r_1^{\text{cal}} = 0.05 + 1.26\ r_1^{\text{exp}}$ with $R^2 = 0.94$. Similar excellent linear correlations have been found previously between the reactivity ratios of the radical pairs benzyl/polystyryl, cyanomethyl/polyacrylonitrilyl, and (methoxycarbonyl)propan-2-yl/polymethyl methacrylyl [2h, j, s].

Experimental. – The arrangements and procedures for steady-state and time-resolved electron spin resonance have been described earlier in detail [2]. The *g* factor of EEst was measured at 295 K relative to that of the *tert*-butyl radical ($g = 2.0026$ [16]) generated from di(*tert*-butyl) ketone in the same soln. The self-termination constant of EEst was determined relative to $2k_t$(*tert*-butyl) in MeCN [17].

*3-Oxoglutaric acid di(*tert*-butyl) ester (=di(*tert*-Butyl) 3-oxopentanedioate; purum* > 97%) was purchased from *Fluka* and *Aldrich*, MeI (> 99% of purity) from *Fluka* and KH, 30% weight in mineral oil suspension, from

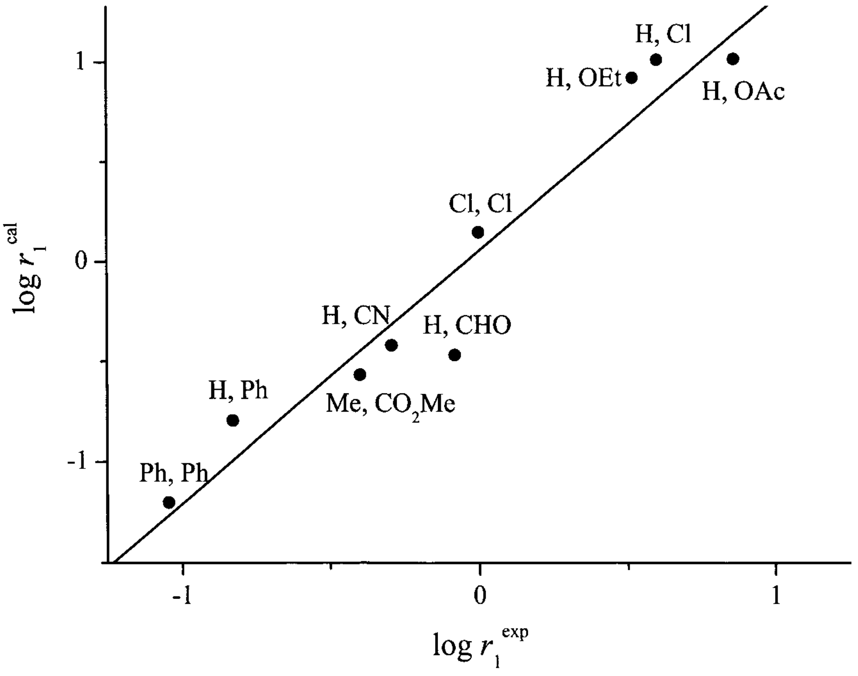

Fig. 5. *Relative rate constants for the addition of the 1-[(*tert*-butoxy)carbonyl]ethyl radical (EEst) to alkenes* vs. *copolymerization parameters* r*₁ of methyl acrylate*

Acros. Solvents of synthetic purity were used as received. ^{1}H-NMR Spectra: *Bruker CXP-200* FT-NMR spectrometer. ^{13}C-NMR Spectra: *Bruker ARX-300* spectrometer. Elemental analyses were kindly provided by the Institute of Organic Chemistry, University of Zurich.

*Synthesis of 2,4-Dimethyl-3-oxoglutaric Acid Di(*tert*-butyl) Ester* (*=(Di(*tert*-butyl) 2,4-Dimethyl-3-oxopentanedioate*). To a suspension of KH (0.13M) in 2 l of THF, a soln. of 3-oxoglutaric acid di(*tert*-butyl) ester (0.8M) in 150 ml of THF was added dropwise at 0–5° during 1 h under N_2. The clear and slightly yellow soln. was stirred for 1 h at r.t. and then cooled to 0°. 150 ml of a soln. of MeI (1.7M) in THF was added dropwise. The soln. became oily and was stirred overnight at r.t. The solvent and solid residues were removed, and the residual oil was distilled at 60° and $2.6 \cdot 10^{-2}$ mbar to provide a colorless liquid ($d(22°) = 0.984$ g/ml) containing both diastereoisomers. Yield: 70%. ^{1}H-NMR ($CDCl_3$, TMS as internal reference, δ in ppm): isomer 1: 3.850 (*q*, $^3J = 6.8$, 1 H); 1.477 (*d*, $^3J = 6.8$, 3 H); 1.347 (*s*, 9 H); isomer 2: 3.607 (*q*, $^3J = 6.8$; 1 H); 1.325 (*d*, $^3J = 6.8$, 3 H); 1.419 (*s*, 9 H). ^{13}C-NMR (C_6D_6, δ in ppm): isomer 1: 201.4 (C=O); 169.3 (COOR); 81.4 (Me_3C), 53.5 (CH); 27.9 (Me of *t*-Bu); 12.9 (Me); isomer 2: 201.9 (C=O), 169.0 (COOR), 81.2 (Me_3C), 52.6 (CH), 27.8 (Me of *t*-Bu); 13.4 (Me). Anal. calc.: C 62.9, H 9.15; found: C 62.7, H 9.38.

We thank the *Swiss National Science Foundation* for financial support and Dr. *A. P. Scott* and Prof. *L. Radom*, Australian National University, Canberra, for the contribution of quantum-chemical results.

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Received June 25, 2001