# Absolute Rate Constants for the Addition of the 2-(Methoxycarbonyl)propan-2-yl and the 3,3,3-Trifluoracetonyl Radicals to Alkenes in Solution

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Absolute rate constants and some of their *Arrhenius* parameters were obtained by time-resolved electron spin resonance (ESR) spectroscopy for the addition of the 2-(alkoxycarbonyl)propan-2-yl and 3,3,3-trifluoroacetonyl (= 3,3,3-trifluoro-2-oxopropyl) radicals to a variety of mono- and 1,1-disubstituted alkenes. Their analysis shows that the addition of 2-(alkoxycarbonyl)propan-2-yl is mainly governed by the exothermicity of the reaction with slight modifications by nucleophilic and electrophilic effects giving rise to an overall ambiphilic behavior. In contrast, large electrophilic polar effects dominate the addition of the 3,3,3-trifluoroacetonyl (= 3,3,3-trifluoro-2-oxopropan-2-yl) radical, as it is expected from its large electron affinity. For both radicals, the activation energies are well-predicted by analytic equations for the enthalpic and polar terms. A comparison of the rate data of 2-(alkoxycarbonyl)propan-2-yl with the homo- and copolymerization rate constants of the propagating radical of methyl methacrylate shows that the additions of these structurally related low- and high-molecular-weight radicals to alkenes are governed by very similar effects.

**1. Introduction.** – Additions of C-centered radicals to C=C bonds are very useful reactions and have many synthetic applications [1]. On variation of radical and substrate, the rate constants change by many orders of magnitude, and, since the beginning of quantitative radical chemistry, this is understood to be caused by a complex interplay of polar, steric, and enthalpic effects [2]. To better separate these effects, we have determined a large number of rate constants and their temperature dependencies for the addition of several C-centered radicals to many mono- and 1,1-disubstituted alkenes in liquid solution by time-resolved electron spin resonance (ESR) and related techniques [3].

Recently, these data led to a comprehensive and predictive analysis [4] in terms of the state or configuration diagram [5]. We showed that, for all additions to mono- and 1,1-disubstituted alkenes, the frequency factors are within narrow ranges, and that, in general, the rate constants increase, and the activation energies decrease with increasing exothermicity of the reaction, as is predicted by the *Evans-Polanyi* relationship. In addition, for many radicals, the activation energies are lowered in a multiplicative way by polar factors which depend on the radical and the alkene substituents. Thus, the easily oxidizable radicals *tert*-butyl ($Me_3\dot{C}$), hydroxymethyl ($\dot{C}H_2OH$), and 2-hydroxypropan-2-yl ($Me_2\dot{C}OH$) show a strong nucleophilic addition behavior towards most alkenes, such that even the omnipresent enthalpic factor is partly obscured. The addition rate constants of the methyl ($\dot{C}H_3$), the benzyl ($Ph\dot{C}H_2$), and the cumyl radical ($Ph\dot{C}Me_2$) follow the reaction enthalpy order more closely and exhibit only weak nucleophilic effects. Enthalpic effects also dominate the additions of the 2-cyanopropan-2-yl ($Me_2\dot{C}CN$), the cyanomethyl ($\dot{C}H_2CN$), and the (*tert*-

butoxycarbonyl)methyl ($\dot{C}H_2CO_2CMe_3$) radical, but these species are also slightly electro- or ambiphilic. Finally, malonyl radicals ($H\dot{C}(CO_2R)_2$) exhibit a clear rate enhancement by electrophilic polar effects as do perfluoroalkyl [6] and dicyanomethyl [7] radicals.

To date, our series included two tertiary radicals with electron-donor substituents ($Me_3\dot{C}$ and $Me_2\dot{C}OH$) but only one tertiary species with an electron-acceptor substituent ($Me_2\dot{C}CN$) and only one type of radical (a cyclic and an open-chain malonyl radical) with a clear electrophilic addition behavior. Therefore, the series was extended here to the addition of 2-(alkoxycarbonyl)propan-2-yl species, namely 2-(methoxycarbonyl)propan-2-yl ($Me_2\dot{C}CO_2Me$) and, for one alkene, the 2-(*tert*-butoxycarbonyl)propan-2-yl ($Me_2\dot{C}CO_2CMe_3$) radical. The latter radicals are also models for the technically important propagating radical of methacrylates. Further, we investigated the addition of the 3,3,3-trifluoroacetonyl (= 3,3,3-trifluoro-2-oxopropan-2-yl) radical ($CF_3CO\dot{C}H_2$) to obtain a further example for a strongly electrophilic radical.

**2. Methods and Results.** – The arrangements and procedures for steady-state and time-resolved ESR have been described in detail in earlier work [3][4].

2.1. *Steady-State Experiments.* 2.1.2. *2-(Methoxycarbonyl)propan-2-yl and 2-(*tert*-Butoxycarbonyl)propan-2-yl.* *tert*-Butyl isobutyrate was synthesized according to a literature procedure [8], but with *N*,*N*-dimethylaniline instead of pyridine as base and omission of the ether solvent. The product was washed five times with 10% (*v*/*v*) $H_2SO_4$, conc. $K_2CO_3$, and $H_2O$, was dried ($CaSO_4$) and found to be sufficiently pure (by GC). The radicals were generated *via* H-atom abstraction by *tert*-butoxy radicals from methyl isobutyrate (*Fluka*, >99% (GC)) and *tert*-butyl isobutyrate (*Eqns. 1* and *2*), and the best results were obtained with solutions of 1.8M distilled di(*tert*-butyl) peroxide (DTPB; *Merck*, $\varepsilon \approx 7\ \text{M}^{-1}\,\text{cm}^{-1}$ at $\lambda \approx 270$ nm, >98% (GC)) in 5.9M methyl isobutyrate or in 4.2M *tert*-butyl isobutyrate.

$$\begin{aligned}&(Me_3CO)_2 + h\nu \rightarrow 2\ Me_3CO^{\bullet}\\&Me_3CO^{\bullet} + R{-}H \rightarrow Me_3COH + R^{\bullet}\end{aligned}\tag{1}$$

At room temperature, the H-abstraction reaction is rather fast ($k_H = 2.5 \cdot 10^5\ \text{M}^{-1}\,\text{s}^{-1}$ [9]), and it was not resolved in time even at lower temperatures. ESR Spectra recorded during steady-state photolysis revealed the expected formation of the radicals $R^{\bullet}$ = 2-(methoxycarbonyl)propan-2-yl and 2-(*tert*-butoxycarbonyl)propan-2-yl by abstraction from the tertiary C-atom of the isobutyrates. The ESR spectra of these radicals are quite complex, because there is a hindered rotation about the $\dot{C}{-}CO$ bond [10] which renders the two Me groups inequivalent, and because of the appreciable second-order splittings. However, for moderate resolution 2-(methoxycarbonyl)propan-2-yl ($Me_2\dot{C}CO_2Me$) shows a simple *septuplet* of *quadruplets* as presented in the inset of *Fig. 1.* The hyperfine coupling constants $a(6\,H_\beta) = (21.58 \pm 0.03)$ G and $a(3\,H_\delta) = (1.25 \pm 0.03)$ G at 294 K compare well with earlier literature data ($g$ = 2.00316, $a(3\,H_{\beta\text{-}cis}) = 21.49$ G, $a(3\,H_{\beta\text{-}trans}) = 21.68$ G, and $a(3\,H_\delta) = 1.29$ G at 233 K [11]). The same holds for 2-(*tert*-butoxycarbonyl)propan-2-yl ($Me_2\dot{C}CO_2CMe_3$) which has an average $a(6\,H_\beta) = (21.51 \pm 0.03)$ G at 294 K ([10]: $g = 2.00329$, $a(3\,H_{\beta\text{-}cis}) =$ 21.44 G, $a(3\,H_{\beta\text{-}trans}) = 21.58$ G at 233 K).The spectra revealed additional small signals arising from photoreduction products of the esters. The concentrations of these side products were at least 20 times lower than those of the dominant radicals, and, therefore, they were neglected in the kinetic analyses. Also, the possible $\beta$-scission of the *tert*-butoxy radical [12] was ignored, because methyl radicals were not detected in the whole temperature range of 233 to 333 K.

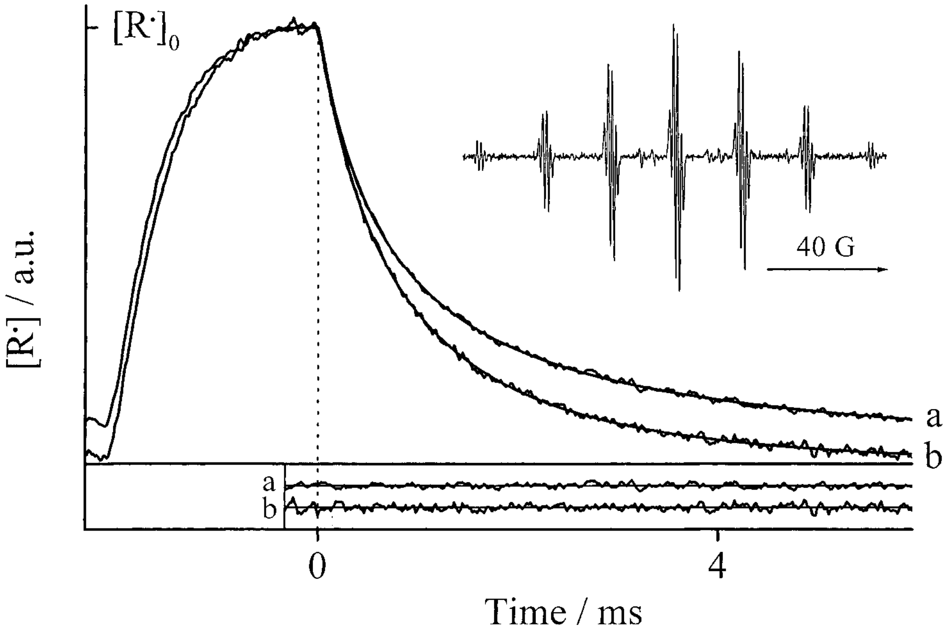

Fig. 1. *Concentration of the 2-(methoxycarbonyl)propan-2-yl radical* vs. *time* a) *in the absence of alkene and* b) *in the presence of 62* mM *acrylonitrile.* Bottom traces are residuals of fits. The inset shows a steady-state ESR spectrum of the radical.

Solutions containing acrylonitrile showed ESR spectra of radicals formed by addition of the ester-derived radicals to the alkene $CH_2$ group. Their magnetic properties, $a(H_\alpha) = 20.04$ G, $a(2\,H_\beta) = 18.60$ G, $a(^{14}N) = 3.40$ G, $g = 2.0027$, and $a(H_\alpha) = 19.85$ G, $a(2\,H_\beta) = 18.61$ G, $a(^{14}N) = 3.37$ G, $g = 2.0028$ for the adducts of 2-(methoxycarbonyl)propan-2-yl and 2-(*tert*-butoxycarbonyl)propan-2-yl, respectively, are typical for the addition products of fairly large radicals [11]. They deserve no further comment, but the radical structures ensure that the addition occurs highly predominantly at the unsubstituted C-atom, as has previously been found for many other radicals [3][4].

2.1.2. *3,3,3-Trifluoroacetonyl.* The radical $CF_3CO\dot{C}H_2$ was generated by photolysis of dibenzoyl peroxide (*Eqn. 3*) and subsequent H-abstraction from trifluoroacetone in 1,1,2-trichloro-1,2,2-trifluoroethane (*Freon 113, Aldrich*, 99%). The best signal-to-noise ratio of the desired radical and minimum side products were obtained with solutions containing 10 mM dibenzoyl peroxide (*Aldrich*, $\varepsilon \approx 2400$ mol$^{-1}$ cm$^{-1}$ at 273 nm) and 1M 1,1,1-trifluoroacetone. Since the $PhCO_2^{\bullet}$ radical decarboxylates within 200 ns [13] the $CF_3CO\dot{C}H_2$ radical is presumably formed by the H-abstraction of the phenyl radical. ESR Spectra recorded during continuous photolysis showed the expected triplet of $CF_3CO\dot{C}H_2$ together with other smaller signals (see inset in *Fig. 4*).

$$(C_6H_5CO_2)_2 + h\nu \rightarrow 2(1-f)C_6H_5CO_2^{\bullet} + 2\,f\,{}^{\bullet}C_6H_5 + 2\,f\,CO_2 \quad f_{298\,K} = 0.29 \tag{3}$$

$$C_6H_5CO_2^{\bullet} \quad \rightarrow {}^{\bullet}C_6H_5 + CO_2 \tag{4}$$

$${}^{\bullet}C_6H_5 + RH \rightarrow C_6H_6 + R^{\bullet} \tag{5}$$

The latter are compatible with the 1,1,2-trifluoro-1,2-dichloroethyl radical [14] formed by Cl-atom abstraction from the solvent by phenyl radicals. These amount to less than 8% of the total signal intensity. Since also only traces of chlorobenzene were found by GC as products in the photolyzed mixture, the Cl-atom abstraction was again neglected in the further analysis. At room temperature, the $CF_3CO\dot{C}H_2$ radical has the coupling constants $a(2\,H_\alpha) = (19.22 \pm 0.05)$ G and $a(3F_\gamma) = (0.58 \pm 0.05)$ G. The $g$ factor $g = 2.0047 \pm 0.0001$ was measured at 297 K with a solution of di(*tert*-butyl) peroxide and 1,1,1-trifluoroacetone in *Freon 113* relative to methyl ($g = 2.0025$ [30]), which appears in the same spectrum. These parameters agree very well with those of other $\alpha$-carbonyl-substituted methyl radicals [11].

Spectra obtained with alkene-containing solutions revealed secondary radicals from additions to the alkene $CH_2$ groups. The adduct to acrylonitrile exhibits a small long-range coupling to two protons which was the same in the presence and the absence of trifluoroacetone in the solution. Hence, the radical is probably the adduct of the phenyl and not of the $CF_3CO\dot{C}H_2$ radical. This means that, in this case, the addition of phenyl to acrylonitrile is faster than the H-abstraction from $CF_3COCH_3$, and the same may be true for the other alkenes. Therefore, the spectra of the adduct radicals did not prove the addition of $CF_3CO\dot{C}H_2$ directly.

2.2. *Time-Resolved Experiments.* 2.2.1. *2-(Methoxycarbonyl)propan-2-yl and 2-(*tert*-Butoxycarbonyl)propan-2-yl. Fig. 1* shows kinetic traces obtained at 294 K for 2-(methoxycarbonyl)propan-2-yl during intermittent photolysis for an alkene free (trace *a*) and for an alkene-containing (trace *b*) solution. According to the usual analysis [3][4], trace *a* is governed by a second-order decay, which is due to radical self-termination ($\tau_2 \approx 800$ µs) and is slightly perturbed by a first- or pseudo-first-order process ($\tau_{10} = (80 \pm 40)$ ms). This is attributed to reactions with the starting compounds and/or products. The same behavior was found for 2-(*tert*-butoxycarbonyl)propan-2-yl in the absence of alkenes. Rate constants for the addition of the 2-(alkoxycarbonyl)-propyl radicals were determined from the pseudo-first-order lifetimes $\tau_1$ obtained for different alkene concentrations. Trace *b* in *Fig. 1* corresponds to an acrylonitrile concentration of 62 mM and led to a shorter $\tau_1 = 5.53$ ms and $\tau_2 = 772$ µs. Plots of $\tau_1^{-1}$ *vs.* the alkene concentrations were linear and lead to the addition rate constants $k_a$ from the slopes. *Fig. 2* shows two examples. The non-zero value of $\tau_1^{-1}$ for $[A] = 0$ represents the side reactions mentioned above. Experiments at different temperatures then gave the activation parameters for the additions by fits of the *Arrhenius* expression to the data (*Fig. 3*).

All results obtained for the 2-(alkoxycarbonyl)propan-2-yl radical are presented in *Table 1*, where the alkenes are ordered according to increasing reactivity. We also give the ranges of the applied alkene concentrations and the number of evaluated kinetic

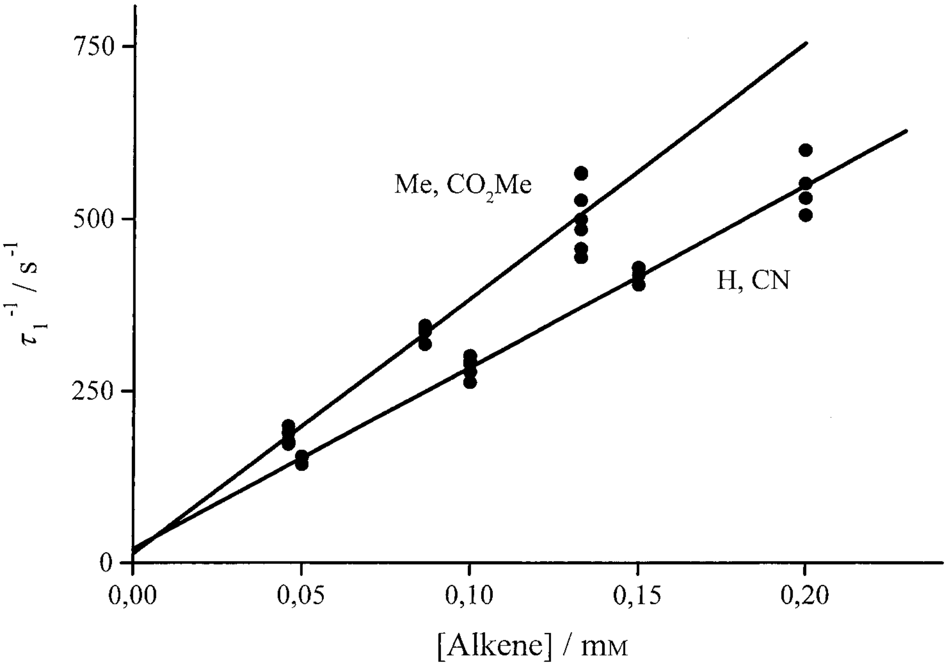

Fig. 2. *Pseudo-first-order plot for the addition of the 2-(methoxycarbonyl)propan-2-yl radical to methyl methacrylate and acrylonitrile at 294 K*

experiments. The addition to several gaseous alkenes of our standard set [3] [4] was not measured, because these were not sufficiently soluble in the present solvent.

2.2.2. *3,3,3-Trifluoroacetonyl.* Kinetic traces obtained during intermittent photolysis in the absence (*a*) and presence (*b*) of an alkene are presented in *Fig. 4*. In trace *a*, the decay is dominated by the second-order self-termination of the radical ($\tau_2 = 500$ μs), which is again slightly perturbed by a slow first- or pseudo-first-order process ($\tau_{10} =$ 14.5 ms). The latter is attributed to a minor reaction of $CF_3CO\dot{C}H_2$ with the solvent and/or the starting compounds. From the life-time $\tau_2$, the rate constant of $CF_3CO\dot{C}H_2$ self-termination at room temperature was obtained as $2k_t(298\ K) = (1.23 \pm 0.05) \cdot 10^{10}$ $M^{-1}\ s^{-1}$ by a standard calibration procedure *vs.* the *tert*-butyl self-termination rate constant of $2k_t(297\ K) = 3.4 \cdot 10^9\ M^{-1}\ s^{-1}$ in tetradecane [15]. The self-termination constant of $CF_3CO\dot{C}H_2$ is similar to that of the $\dot{C}H_3$ radical in the same solvent $2k_t(298\ K) = (1.65 \pm 0.2) \cdot 10^{10}\ M^{-1}\ s^{-1}$ [30], and it is on the order of magnitude expected for a diffusion-controlled process.

With alkene present (*Fig. 4*, trace *b*), the first-order life-time decreases as expected from the addition reaction. As before, the addition rate constants were determined from the slopes of the linear plots of $\tau_1^{-1}$ *vs.* the alkene concentrations, and examples are given in *Fig. 5*. Unfortunately, for this radical, the temperature dependence could not be measured, because the low boiling points of the solvent and of trifluoroacetone prevented measurements at elevated temperatures, whereas dibenzoyl peroxide was found to be not sufficiently soluble below room temperature. *Table 2* shows the rate constants, the number of evaluated kinetic traces, and the variation range of the alkene concentration.

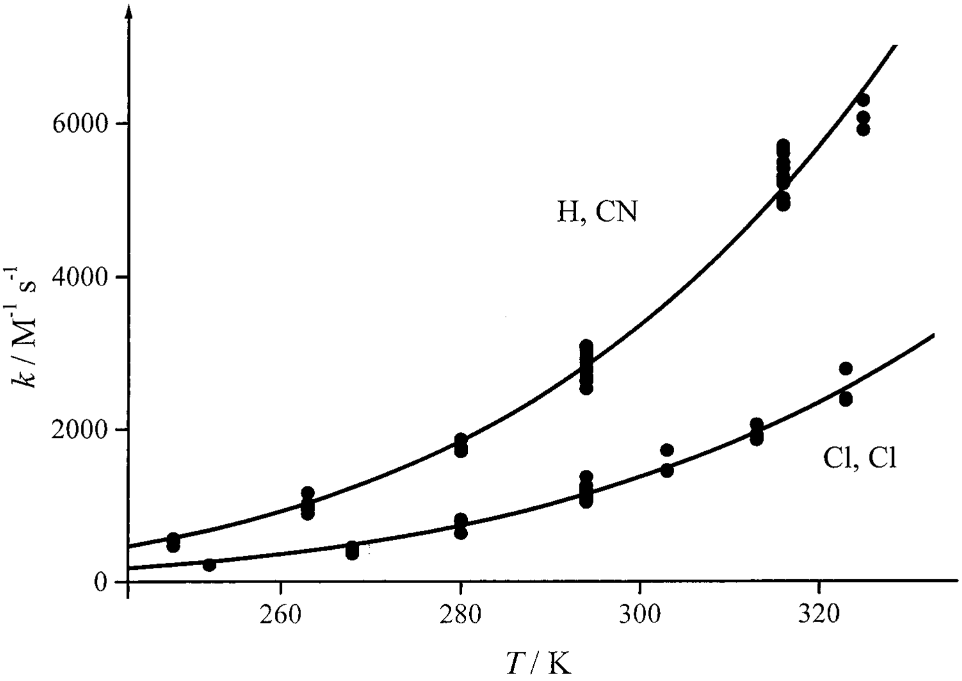

Fig. 3. *Rate constants for the addition of the 2-(methoxycarbonyl)propan-2-yl radical to acrylonitrile and to 1,1-dichloroethene at various temperatures and fits to the* Arrhenius *law*

**3. Analysis and Discussion.** – 3.1. *Rate Constants.* Apart from the propagation rate constants and the copolymerization parameters of methyl methacrylate, which are related to the addition rate constants of the 2-(alkoxycarbonyl)propan-2-yl radicals, and which are discussed later, there are only very few literature data with which our rate constants can be compared. *Gilbert et al.* [16] used an indirect steady-state ESR method to measure the addition rate constant of the 2-carboxypropan-2-yl radical ($Me_2\dot{C}CO_2H$) to acrylic and methacrylic acid at pH 2 in $H_2O$ and at room temperature. They report $k = 5 \cdot 10^5$ M$^{-1}$ s$^{-1}$ and $k = 7 \cdot 10^5$ M$^{-1}$ s$^{-1}$, respectively, and these values are by more than two orders of magnitude larger than our results (*Table 1*). Though $H_2O$ as a solvent normally accelerates additions in comparison to less polar media [3o][4b], and the different radical and alkene substitutions may also cause slight changes of the rate constants, we believe that the results of *Gilbert et al.* are not very likely to be tenable. The order of magnitude of their findings disagrees not only with ours but also with that expected for the addition rate constants of the propagating radical of methyl methacrylate (*vide infra*). For $CF_3CO\dot{C}H_2$ and related species there are not earlier addition rate data.

A comparison of the rate constants of the 2-(alkoxycarbonyl)propan-2-yl radicals of *Table 1* with those of other radicals in our series [3][4] shows that these radicals are only moderately selective, since the rate constants at room temperature vary with alkene substitution by only a factor of 550. Overall, their reactivity is also

Table 1. *Absolute Rate Constants* ($k$) *at* ($294 \pm 1$) *K*, *Frequency Factors* ($A$), *and Activation Energies* ($E_a$) *for the Addition of the 2-(Methoxycarbonyl)propan-2-yl Radical to Alkenes* ($CH_2{=}CXY$)

| X | Y | $c$ [mM]<br>(T [K]) | $n$ | $k$ [$M^{-1}\ s^{-1}$][a]) | $E_a$ [kJ $mol^{-1}$][a])[b]) | $\log(A/M^{-1}\ s^{-1})$[a]) |
|---|---|---|---|---|---|---|
| H | AcO | 1.0–4.0 | 14 | 18 (3) | 35.6 | |
| Me | MeO | 1.28 | 8 | 50 (25) | 33.1 | |
| Me | AcO | 2.0–4.0 | 13 | 58 (2) | 32.7 | |
| H | EtO | 1.0–4.0 | 12 | 75 (25) | 32.1 | |
| H | $Me_3Si$ | 1.0–2.0 | 12 | 75 (20) | 32.1 | |
| Me | Cl | 0.5–1.0 | 10 | 150 (35) | 30.4 | |
| H | $CO_2Me$ | 0.125–0.400<br>(255–315) | 39 | 1150 (70) | 19.8 (12)<br>25.3 | 6.6 (+2/−3) |
| Cl | Cl | 0.239–0.487<br>(253–323) | 34 | 1170 (30) | 21.9 (8)<br>25.3 | 6.9 (+1/−) |
| H | CHO | 0.050–0.110 | 10 | 1800 (300) | 24.2 | |
| H | CN | 0.050–0.200<br>(248–325) | 23 | 2650 (100)<br>23.3 | 21.0 (4) | 7.2 (+1/−1) |
| Me | $CO_2Me$ | 0.046–0.133 | 17 | 3710 (250)22.4 | | |
| Me | CN | 0.025–0.100 | 15 | 4450 (200) | 22.0 | |
| H | Ph | 0.050–0.100<br>(253–318) | 13 | 5500 (400) | 16.5 (12)<br>21.5 | 6.7 (+3/−3) |
| Me | Ph | 0.041–0.110 | 20 | 6050 (250) | 21.2 | |
| Ph | Ph | 0.010–0.033<br>(251 – 323) | 13 | 10200 (450) | 16.6 (5)<br>20.0 | 7.0 (+1/−1) |
| H | CN[c]) | 0.069–0.083<br>(295–315) | 23 | 4400 (200) | 21.8 (10)<br>21.8 | 7.5 (+2/−2) |

[a]) Standard deviations in units of the last digital number are given in brackets. [b]) Activation energies without errors were calculated from the rate constants with $\log(A/M^{-1}\ s^{-1}) = 7.5$. [c]) Addition of the 2-(*tert*-butoxycarbonyl)propan-2-yl radical.

rather low. It is slightly higher than, but closely resembles, that of the 2-cyanopropan-2-yl radical, is higher than that of the resonance-stabilized benzyl radical, and is considerably lower than that of the (*tert*-butoxycarbonyl)methyl and the methyl radicals.

The addition rate constants of $CF_3CO\dot{C}H_2$ vary with alkene substitution by a factor of about 250, *i.e.*, this radical is also not very selective. However, its reactivity is high. It resembles that of the malonyl radical, and to most alkenes the $CF_3CO\dot{C}H_2$ radical adds even faster than the $\dot{C}H_3$ radical. From the substitution of the radicals and in view of our earlier experience, these trends are reasonable, and they will be analyzed in the following in greater detail.

3.2. *Frequency Factors. Table 1* reveals that the frequency factors for the addition of the 2-(alkoxycarbonyl)propan-2-yl radicals alkenes are all in the narrow range of $6.6 < \log(A/M^{-1}\ s^{-1}) < 7.5$ and show no specific dependence on the alkene substituents. Therefore, as also found for other radicals [3][4], the spread is presumably caused by error-compensation effects of the *Arrhenius* parameters. The average frequency factor is $\log(A/M^{-1}\ s^{-1}) = 7.0 \pm 0.3$. Within the error limits, this is within the average of $\log(A/M^{-1}\ s^{-1}) = 7.5 \pm 0.8$, suggested earlier for tertiary radicals [3][4], and ensures the general validity of the latter value. To obtain the activation energies for all alkenes of *Table 1* from the rate constants, the average $\log(A/M^{-1}\ s^{-1}) = 7.5$ was used.

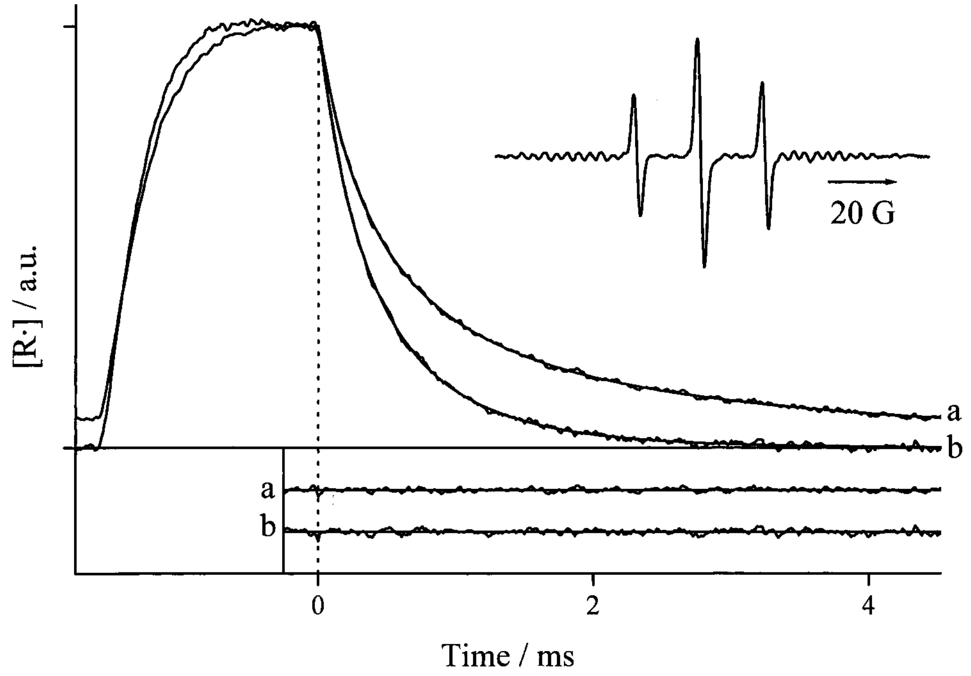

Fig. 4. *Concentration of the 3,3,3-trifluoroacetonyl radical* vs. *time* a) *in the absence of alkene and* b) *in the presence of 3.7* mM *trimethyl(vinyl)silane.* Bottom traces are residuals of fits. The inset shows a steady-state ESR spectrum of the radical.

For $CF_3CO\dot{C}H_2$ additions, the frequency factors could not be measured. However, in previous studies [3][4], we have established an average frequency factor for the addition of primary radicals to alkenes as $\log(A/\text{M}^{-1}\,\text{s}^{-1}) = 8.5 \pm 0.3$, and have now used this value to convert the rate data of *Table 2* to activation energies for further discussion.

That the frequency factors are similar within one order of magnitude indicates rather similar transition-state structures for the various additions, as is also known from theoretical work [17]. While the newly forming bond is still long (210–240 pm), the angle of attack is already tightly prescribed, and there is a considerable out-of-plane deformation at the two newly bonded C-atoms. Moreover, the dependence of the frequency factors on radical structure that emerged from the data is also reasonable. The tertiary radicals should loose more motional freedom than primary radicals on approach to the transition structure, because the rotation of methyl or other substituent groups becomes more hindered. This provides a more negative activation entropy for the tertiary radicals in comparison to the primary species and, hence, the lower frequency factor.

3.3. *Activation Energies.* The narrow range of the frequency factors for the additions means that the variation of the rate constants with the alkene substitution is to the larger part due to variations of the activation energy. Previously, this has also been found for other C-centered radicals [3][4]. To rationalize the individual substituent effects, we shall now seek correlations of the activation energies with the reaction

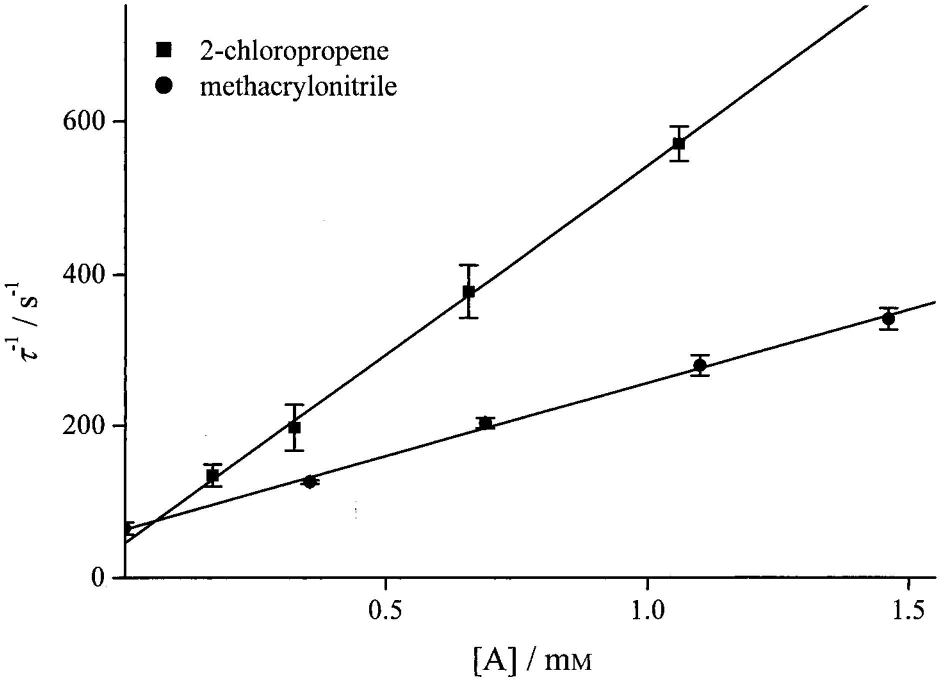

Fig. 5. *Pseudo-first-order plot for the addition of the 3,3,3-trifluoroacetonyl radical to 2-chloropropene and methacrylonitrile at 295 K*

Table 2. *Absolute Rate Constants for the Addition of the 3,3,3-Trifluoroacetonyl Radical to Alkenes* ($CH_2=CXY$) *in* Freon 113 *at* ($296 \pm 1$) *K*

| X | Y | $c$ [mM] | $n$ | $k$ [$10^4$ M$^{-1}$ s$^{-1}$][a]) | $E_a$ [kJ mol$^{-1}$][b]) |
|---|---|---|---|---|---|
| H | CN | 1.5–6.0 | 14 | 3.5 (3) | 22.6 |
| H | H | 1.1–4.7 | 20 | 3.9 (2) | 24.0 |
| H | CHO | 1.4–6.4 | 17 | 6.4 (6) | 21.1 |
| H | Cl | 0.9–3.4 | 15 | 9.5 (2) | 20.1 |
| H | $CO_2Me$ | 0.9–3.7 | 15 | 12.5 (5) | 19.3 |
| H | Me | 0.7–2.3 | 24 | 19 (1) | 18.4 |
| Me | CN | 0.4–1.5 | 16 | 19 (1) | 18.4 |
| H | AcO | 0.5–2.2 | 15 | 20 (7) | 18.3 |
| H | $Me_3Si$ | 0.9–2.2 | 14 | 21 (1) | 18.1 |
| H | Et | 0.5–1.9 | 23 | 28 (1) | 17.4 |
| Cl | Cl | 0.3–1.1 | 27 | 33 (2) | 17.0 |
| Me | Cl | 0.2–1.1 | 20 | 50 (2) | 16.0 |
| Me | AcO | 0.2–0.8 | 19 | 59 (3) | 15.3 |
| Me | $CO_2Me$ | 0.1–0.8 | 19 | 120 (60) | 13.8 |
| Me | Me | 0.04–0.18 | 12 | 400 (10) | 10.8 |
| H | Ph | 0.02–0.09 | 13 | 630 (70) | 9.7 |
| Ph | Ph | 0.02–0.09 | 17 | 690 (30) | 9.5 |
| Me | Ph | 0.01–0.13 | 14 | 770 (60) | 9.2 |

[a]) Standard deviations in units of the last digital number are given in parenthesis. [b]) Calculated from the rate constants with $\log(A/\mathrm{M}^{-1}\,\mathrm{s}^{-1}) = 8.5$.

enthalpies $H_r$ and, for polar effects, with the radical- and alkene-ionization energies *IE* and electron affinities *EA*. Steric effects of the alkene substituents on the activation energies are not considered, since they should be small for additions at the unsubstituted carbon, and an inspection of the data does not reveal any trends.

In our earlier analysis [4b] of many data for the addition of C-centered radicals to mono- and 1,1-disubstituted alkenes, which included those presented here, we have shown that the activation energies $E_a$ are well-described by *Eqn. 6*.

$$E_a = (50 + 0.22\, H_r)\, F_n F_e \qquad (6)$$

The first term in brackets represents the *Evans-Polanyi* relationship, according to which the activation energy decreases with increasing exothermicity ($-H_r$) of the addition. It describes the activation energies alone where polar effects are absent and is an upper limit. The polar factors $F_n$ and $F_e$ ($0 < F_{n,e} < 1$) decrease the activation energy. The nucleophilic part $F_n$ depends on the energy gap between the ground-state configuration of the reactants (RA, where R denotes the radical and A the alkene) and the charge-transfer configuration $R^+A^-$ reduced by a *Coulomb* interaction in the transition state geometry $C_n$, *i.e.*, on $IE(R) - EA(A) - C_n$, and on an interaction parameter $\gamma_n$ between the configurations. Its electrophilic analog $F_e$ ($0 < F_e < 1$) depends on $IE(A) - EA(R) - C_e$ and a corresponding interaction parameter $\gamma_e$. Both polar factors $F_n$ and $F_e$ are restricted to values between 0 and 1, because the polar effects can only reduce the reaction barriers. As reasonable functions for $F_n$ and $F_e$, we have suggested *Eqns. 7* and *8* and have presented suitable ranges for the parameters *C* and $\gamma$ [4b].

$$F_n = 1 - \exp\left[-((IE(R) - EA(A) - C_n)/\gamma_n)^2\right] \qquad (7)$$

$$F_e = 1 - \exp\left[-((IE(A) - EA(R) - C_e)/\gamma_e)^2\right] \qquad (8)$$

Moreover, it has been pointed out [4] that the energies $H_r$, $EA(A)$, and $IE(R)$ are themseves interrelated. Thus, substituents that make an alkene electron-deficient and increase the alkene electron affinity often also stabilize the resulting adduct radical, *i.e.*, render the reaction more exothermic. On the other hand, substituents that make alkenes more electron-rich and decrease their ionization energies often decrease the exothermicity. Nucleophilic radicals have low ionization energies. For these the effects of alkene substituents that increase the exothermicity (enthalpic effect) and simultaneously increase the electron affinity (polar effect) reinforce each other. Hence, nucleophilic radicals are generally highly selective and also particularly reactive towards the electron-deficient alkenes. Electrophilic radicals have high electron affinities. For these, the favorable polar effect runs opposite to favorable enthalpic substituent effects. Therefore, the radicals are not very selective. However, they are more reactive than radicals that exhibit only the same enthalpic effects, since $F_e$ is smaller than one. Radicals that are on the borderline of a nucleophilic and an electrophilic behavior may exhibit an ambiphilic nature and react particularly fast with both strongly electron-deficient and electron-rich alkenes.

In a schematic way, *Fig. 6* shows how the nature of the species reveals itself in a plot of the activation energies with the reaction enthalpy. It must also be mentioned that in such plots the Ph-substituted alkenes are often outlyers if the polar effects are important. They show higher activation energies than other compounds with similar reaction enthalpies, similar ionization energies, and electron affinities, because the charge delocalization in the transition structure diminishes both the *Coulomb* attraction $C$ and the interaction parameters $\gamma$, and this leads to smaller rate enhancements by polar effects.

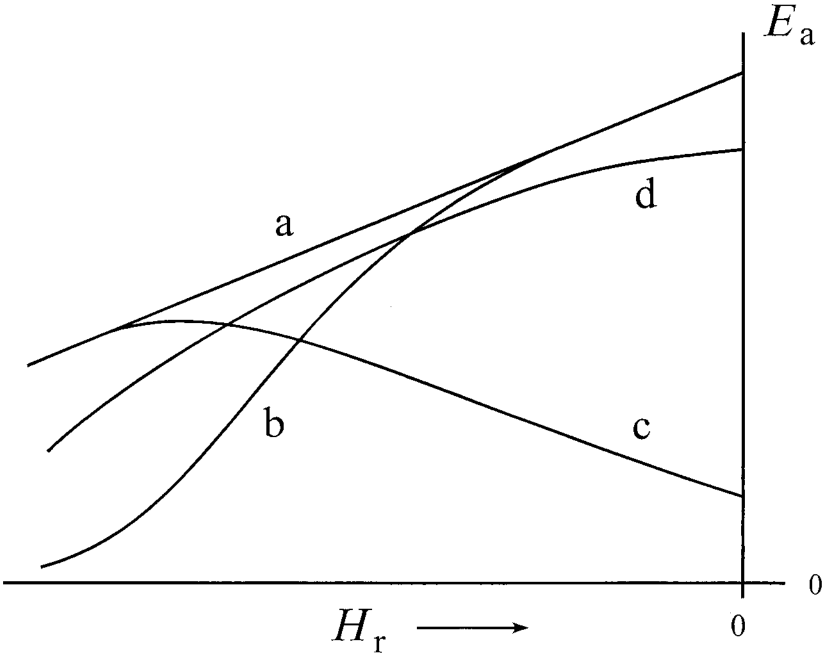

Fig. 6. *Schematic representation of the dependence of the activation energy* $E_a$ *on the reaction enthalpy* $H_r$ *for the addition of alkyl radicals to mono- and 1,1-disubstituted alkenes for* a) *pure enthalpy control, and additional* b) *nucleophilic*, c) *electrophilic*, *and* d) *ambiphilic polar effects*

To apply *Eqn. 6*, the reaction enthalpies $H_r$ of the addition step have to be known. As before [3][4], they have been estimated, because experimental data are not available. We consider the reaction sequence in *Eqn. 9*, from which the reaction enthalpy can be written as a combination of molar heats of formation, $h_f$, and bond dissociation energies, *BDE*, of stable compounds (*Eqn. 10*), where A stands for the alkene. It is obvious from *Eqn. 10* that it includes the effects of stabilization of the attacking and resulting radical and of the alkene. Values for $h_f$(RAH) and *BDE*(RA–H) are known for many compounds with the residue methyl (R=CH$_3$) but not for the radicals considered here. Therefore, we start from the most recent and re-evaluated values of $H_r$ [3o] for $\dot{C}H_3$ radical additions to the alkenes and increment these for the substitution of methyl by 2-(methoxycarbonyl)propan-2-yl and

$$\mathrm{R-H + CH_2{=}CXY \rightarrow \dot{R} + \dot{H} + CH_2{=}CXY \rightarrow \dot{H} + RCH_2\dot{C}XY \rightarrow RCH_2CHXY} \quad (9)$$

$$H_r(\dot{\mathrm{R}}) = h_f(\mathrm{RAH}) - h_f(\mathrm{RH}) - h_f(\mathrm{A}) + BDE(\mathrm{RA{-}H}) - BDE(\mathrm{R{-}H}) \quad (10)$$

$CF_3CO\dot{C}H_2$, *i.e.*, according to *Eqn. 11*. This procedure implies that $BDE(RA-H)$ is not influenced by the added radical $\dot{R}$.

$$H_r(\dot{R}) = H_r(\dot{C}H_3) + h_f(RA-H) - h_f(CH_3AH) - h_f(RH) + h_f(CH_4) - BDE(R-H) + BDE(CH_3-H) \quad (11)$$

For the estimation of the $H_r$ value for addition of the 2-(methoxycarbonyl)propan-2-yl radical to ethene, the following (gas phase) standard heats of formation are available [18]: $CH_4$: $-74.5$ kJ mol$^{-1}$, $CH_3CH_2CH_3$: $-104.5$ kJ mol$^{-1}$, $(CH_3)CHCO_2CH_3$: $-456$ kJ mol$^{-1}$, but $h_f$ seems to be unknown for $CH_3CH_2C(CH_3)_2CO_2CH_3$. It can be estimated as $-511$ kJ mol$^{-1}$ from the tabulated $h_f((CH_3)_3CCO_2CH_3) = -491$ kJ mol$^{-1}$ by addition of the increment of $-20$ kJ mol$^{-1}$ for substitution of a Me by an Et group, which was derived [3o] from various related pairs of molecules found in [18]. The bond dissociation energies are 439 kJ mol$^{-1}$ for $CH_3-H$ [19] and 379 kJ mol$^{-1}$ for $H-C(CH_3)_2CO_2CH_3$ [30]. Insertion of these data into *Eqn. 11* shows that the addition of 2-(methoxycarbonyl)propan-2-yl radical to ethene is by 35 kJ mol$^{-1}$ less exothermic than that of $\dot{C}H_3$. This difference is assumed to hold also in solution and for the other alkenes. Of course, the estimation procedure leads to errors which may be as large as 10 kJ mol$^{-1}$. However, the low exothermicity of the additions immediately suggests a rather low reactivity of 2-(alkoxycarbonyl)propan-2-yl radicals as it is observed.

For $CF_3CO\dot{C}H_2$, the same procedure was applied to obtain $H_r$ values for the addition to ethene: $h_f(CF_3COCH_3) = -812$ kJ mol$^{-1}$ is known [18], and $BDE(H-CH_2COCF_3) = 408$ kJ mol$^{-1}$ was calculated according to the procedure of *Cumming* and *Kebarle* [20]. $h_f(CF_3COCH_2CH_2CH_3) = -853.7$ kJ mol$^{-1}$ was obtained from $h_f(CF_3COCH_3)$ and from the difference of $-41.7$ kJ mol$^{-1}$ between the heats of formation of $CH_3COCH_3$ and $CH_3COCH_2CH_2CH_3$ [18]. With the data given above for $CH_4$ and $CH_3CH_2CH_3$, and *Eqn. 11*, these energies render the addition of $CF_3CO\dot{C}H_2$ to ethene by 16 kJ mol$^{-1}$ less exothermic than that of $\dot{C}H_3$. Again, this difference in $H_r$ was assumed to hold also for the other alkenes, and the small difference with $\dot{C}H_3$ allows in part for the observed rather high rate constants of $CF_3CO\dot{C}H_2$ additions.

To discuss the polar factors, we also need the ionization energies, *IE*, and the electron affinities, *EA*, of the alkenes and of the radicals. For the alkenes, these data have been listed in our earlier work [3o]. For 2-(methoxycarbonyl)propan-2-yl and $CF_3CO\dot{C}H_2$, the *IE*s and *EA*s were calculated by a high-level *ab initio* procedure as $IE = 7.7$ eV, $EA = 1.34$ eV, and $IE = 10.9$ eV, $EA = 3.18$ eV, respectively [21], and, for $CF_3CO\dot{C}H_2$, an experimental value of $EA = 2.625$ eV is also available [22]. In comparison to other radicals [3][4], the 2-(methoxycarbonyl)propan-2-yl radical has an *IE* which is larger than that of strongly nucleophilic radicals, such as 6.7 eV for *tert*-butyl, and an *EA* lower than those of strongly electrophilic species, such as 1.8 eV for malonyl. Hence, the addition reactions of this radical should not be subject to very strong polar effects. On the other hand, the *EA* of $CF_3CO\dot{C}H_2$ is larger than that of the electrophilic malonyl radical (1.8 eV), and therefore large electrophilic polar effects are expected. In combination with the high exothermicity, this explains why trifluoroacetonyl is often even more reactive than the methyl radical.

*Fig. 7* shows the activation energies calculated from the rate constants as described above for the addition of the 2-(methoxycarbonyl)propan-2-yl radical and plotted against the reaction enthalpies. Also shown is the line expected from *Eqn. 6* for complete enthalpy control and negligible polar effects. A linear correlation of the data with the reaction enthalpies gave $E_a$/kJ mol$^{-}$1 = 47.9(3.0) + 0.24(0.03)$H_r$/kJ mol$^{-1}$ ($r$ = 0.87), which is very reasonable and not far from the general *Evans-Polanyi* line. Clearly, and in view of the error limits of the experimental data and the estimated reaction enthalpies, the activation energies point to a dominant enthalpy control. No correlation was found between $E_a$ or log ($k$) and the alkene ionization energies, which excludes large electrophilic polar effects, but there is also a reasonable correlation with the alkene electron affinities which is probably caused by the interrelation of $H_r$ and $EA$. However, in *Fig. 7* there are noticeable deviations from the ideal line to lower values for both the strongly electron-deficient (*e.g.*, methyl methacrylate, methacrylonitrile) and the electron-rich alkenes (ethoxyethene, 2-methoxypropene). This means additional polar effects, and the comparison of *Fig. 7* with *Fig. 6* suggests that the general addition behavior can be termed ambiphilic. Yet, the polar effects are small and decrease the activation energies by less than 10 kJ mol$^{-1}$.

The corresponding plot of $E_a$ *vs.* $H_r$ for $CF_3CO\dot{C}H_2$ is shown in *Fig. 8*. Now the deviations from the line expected for complete enthalpy control are larger, and they are particularly large for electron-rich alkenes such as 2-methylpropene. If the Ph-substituted alkenes are disregarded, since they should lead to weaker polar effects, the

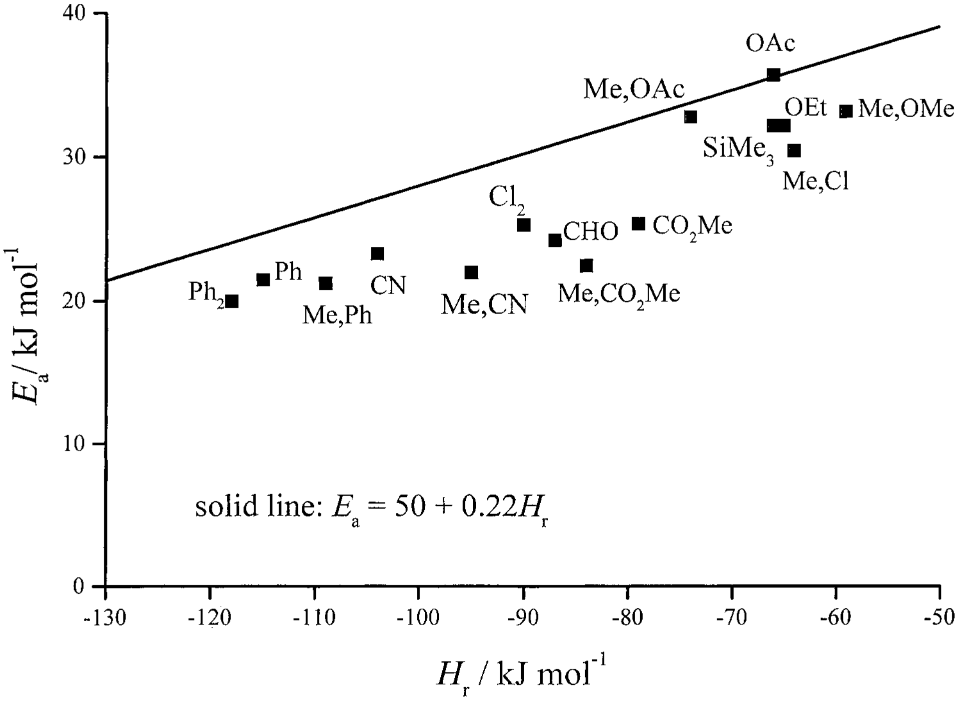

Fig. 7. *Activation energies* $E_a$ *for the addition of the 2-(methoxycarbonyl)propan-2-yl radical to alkenes as a function of the reaction enthalpy* $H_r$. Solid line as expected for complete enthalpy control.

trend of the deviations follows that predicted in *Fig. 6* for an electrophilic addition behavior. This agrees with the large *EA* of the radical and is supported by a very reasonable correlation of log ($k$) with the alkene *IE*s. Division of the activation energies by the enthalpy term of *Eqn. 6* gives the electrophilic factor $F_e$. This is plotted in *Fig. 9* against the energy gap between the ground-state (RA) and the charge-transfer configuration ($R^-A^+$). Also shown are lines calculated with *Eqn. 8* and appropriate *Coulomb* and interaction terms, which accommodate the data and are given in *Fig. 9*. In comparison with other radicals [4b], the parameters are reasonable, and, as expected, the weaker polar effects for Ph-substituted alkenes manifest themselves in smaller *Coulomb* and interaction terms.

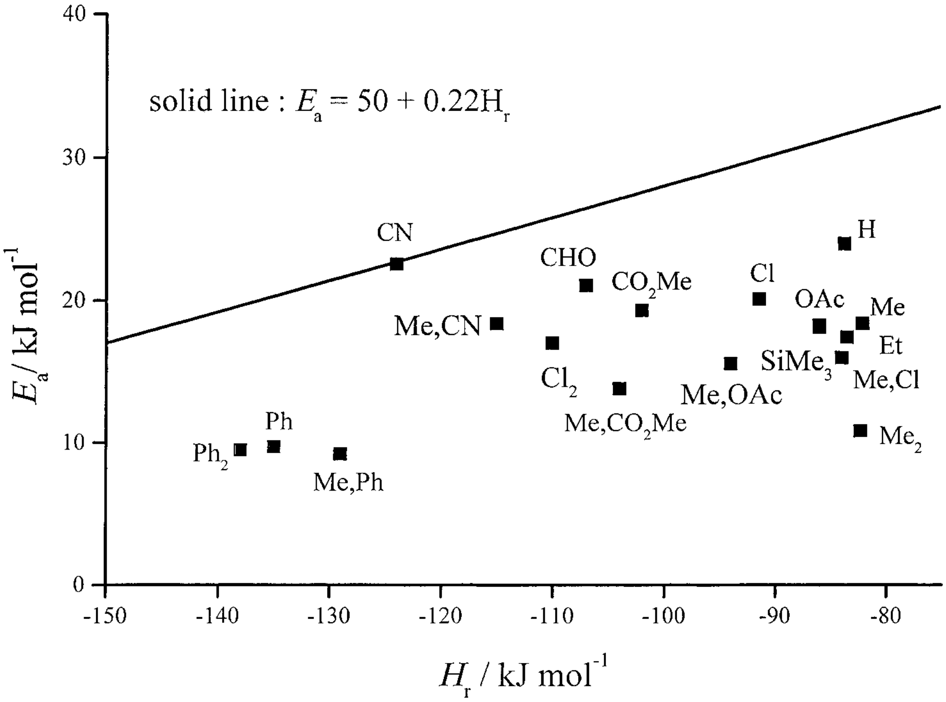

Fig. 8. *Activation energies* $E_a$ *for the addition of the 3,3,3-trifluoroacetonyl radical to alkenes as a function of the reaction enthalpy* $H_r$. Solid line as expected for complete enthalpy control.

Finally, we have calculated the activation energies with *Eqns. 6* and *7*. For $CF_3CO\dot{C}H_2$, the parameters $C_e$ and $\gamma_e$ were as given in *Fig. 9*, and the experimental electron affinity was used. For the polar effects of 2-(methoxycarbonyl)propan-2-yl, we used $C_n = 6$ eV, $\gamma_n = 1.5$ eV, and $C_e = 4.5$ eV, $\gamma_e = 2$ eV for the non-Ph-substituted, and smaller values $C_n = 5.5$ eV, $\gamma_n = 0.75$ eV, and $C_e = 4$ eV, $\gamma_e = 2$ eV for the Ph-substituted alkenes. These parameters are similar to those found for other radicals [4b], and the comparison of the calculated and experimental activation energies in *Fig. 10* demonstrates the equations, and the parameters describe the data within a maximum deviation of *ca.* 5 kJ mol$^{-1}$.

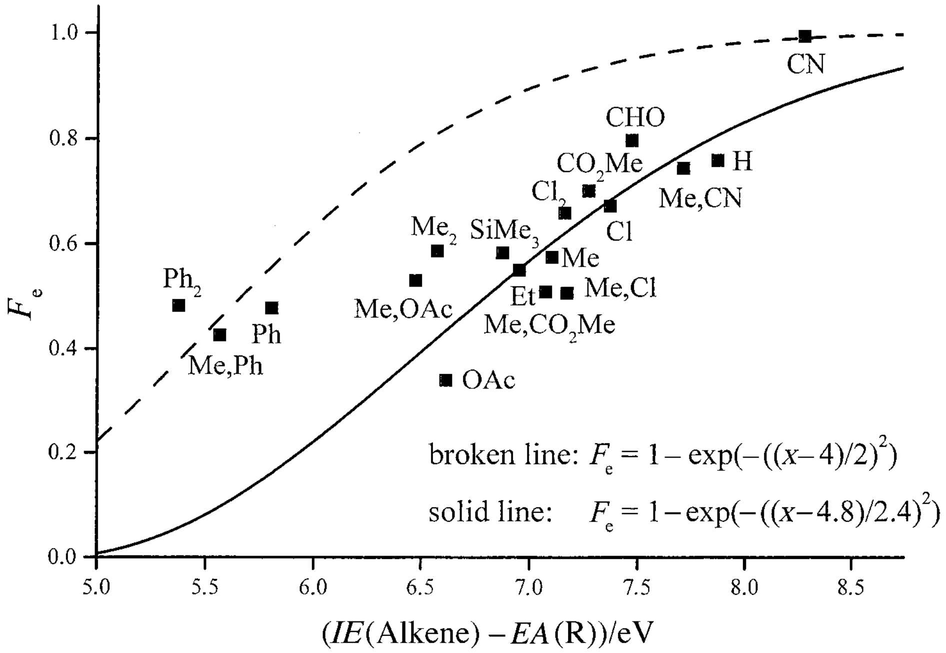

Fig. 9. *Electrophilic polar factor* $F_e$ *for the addition of the 3,3,3-trifluoroacetonyl radical to alkenes*

In conclusion, the addition of 2-(alkoxycarbonyl)propan-2-yl radicals to alkenes is mainly governed by the reaction enthalpy. It is comparatively slow because there is a considerable radical stabilization, but there are also slight ambiphilic polar effects. The $CF_3CO\dot{C}H_2$ radical adds to alkenes rather fast, because there is little radical stabilization, *i.e.*, the exothermicity is high, and, for many alkenes, the reactions are additionally facilitated by strong electrophilic polar effects. With reasonable parameters, the predictive equations developed in an earlier analysis [4b] describe the activation energies rather well.

3.4. *2-(Methoxycarbonyl)propan-2-yl and the Propagating Radical of Methyl Methacrylate.* The 2-(methoxycarbonyl)propan-2-yl ($Me_2\dot{C}CO_2Me$) radical is structurally related to the propagating radical of methylmethacrylate ($RCH_2\dot{C}(CH_3)CO_2CH_3$, R = polymer chain), and it is expected that the reactivities of these two radicals are related. Recently, the homopropagation rate constant of methyl methacrylate has been critically assessed [23]. Its temperature dependence is governed by $\log(A/\text{M}^{-1}\,\text{s}^{-1}) = 6.43$ and $E_a = 22.36$ kJ mol$^{-1}$ and leads to a rate constant $k = 287$ M$^{-1}$ s$^{-1}$ at 294 K. 2-(Methoxycarbonyl)propan-2-yl adds to methyl methacrylate with $\log(A/\text{M}^{-1}\,\text{s}^{-1}) = 7.5$, $E_a = 22.4$ kJ mol$^{-1}$ and $k_{294} = 3710$ M$^{-1}$ s$^{-1}$ (*Table 1*). Obviously, the activation energies of the two additions are very similar, but the frequency factor and the rate constant are lower for the polymer radical, and this remains also valid when the uncertainties of our activation parameters (2.8 kJ mol$^{-1}$ for $E_a$ and 0.5 for log ($A$)) are considered. There is evidence for polymeric radicals that the propagation constants decrease substantially with increasing chain length [23]. This is confirmed by the present findings, and the

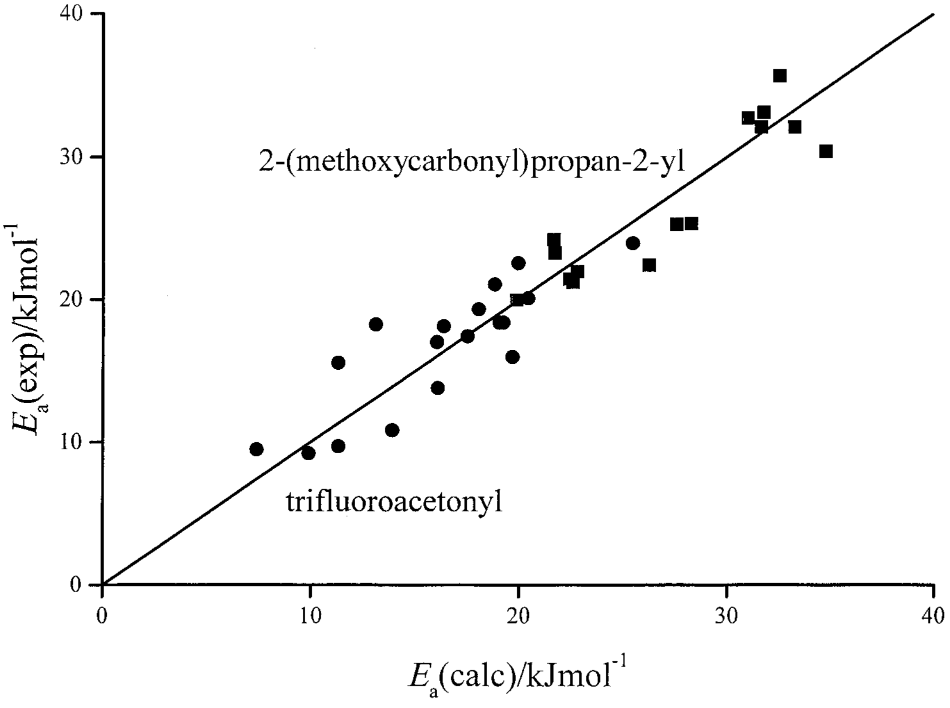

Fig. 10. *Experimental* vs. *calculated activation energies for the addition of the 2-(methoxycarbonyl)propan-2-yl radical* (squares) *and of the 3,3,3-trifluoroacetonyl radical* (circles) *to alkenes.* Solid line represents $E_a$(exp) = $E_a$(calc).

similarity of the activation energies indicates moreover that the chain-length effect may be primarily due to a decreasing frequency factor [24].

Further, one can compare the ratios of rate constants for the addition of the 2-(methoxycarbonyl)propan-2-yl radical to different alkenes with the co-polymerization parameters $r_1$ of methyl methacrylate. These are defined as $r_1 = k_p/k_a$, where $k_p$ is the rate constant for the addition of the propagating radical to methyl methacrylate, and $k_a$ holds for the addition to another monomer. Many co-polymerization parameters of methyl methacrylate are available [25], but, for several monomers, they show a considerable spread, and reasonable averages had to be chosen for a comparison. *Fig. 11* shows a plot of log($r_1$) *vs.* relative rate constants of 2-(methoxycarbonyl)propan-2-yl ($k$(methacrylate))/$k$(alkene)) as calculated from the data of *Table 1*. There is an excellent linear correlation which demonstrates that the additions of the two radicals are governed by the same (enthalpic and polar) factors. 1,1-Diphenylethene is an obvious exception, and a redetermination of the rather early value of $r_1$ for this alkene [26] seems now necessary.

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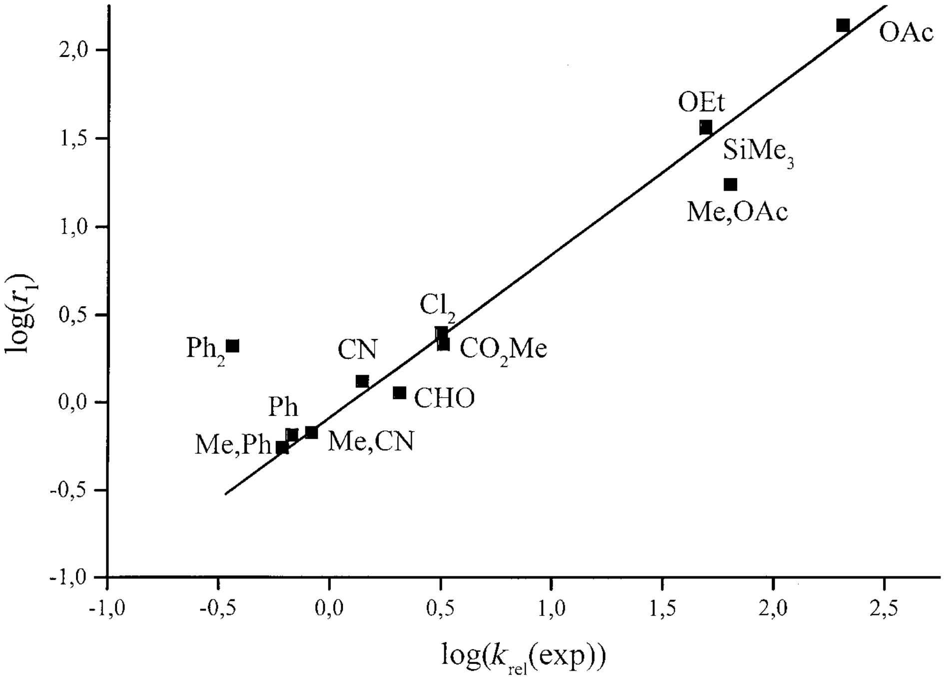

Fig. 11. *Experimental co-polymerization parameters of methyl methacrylate* vs. *relative rate constants of the 2-(methoxycarbonyl)propan-2-yl radical*

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