16. Absolute Rate Constants for the Addition of Cyanomethyl ($\cdot CH_2CN$) and (*tert*-Butoxy)carbonylmethyl ($\cdot CH_2CO_2C(CH_3)_3$) Radicals to Alkenes in Solution

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(8.XI.94)

Absolute rate constants and their temperature dependence were determined by time-resolved electron spin resonance for the addition of the radicals $\cdot CH_2CN$ and $\cdot CH_2CO_2C(CH_3)_3$ to a variety of mono- and 1,1-disubstituted and to selected 1,2- and trisubstituted alkenes in acetonitrile solution. To alkenes $CH_2{=}CXY$, $\cdot CH_2CN$ adds at the unsubstituted C-atom with rate constants ranging from $3.3 \cdot 10^3$ $M^{-1}s^{-1}$ (ethene) to $2.4 \cdot 10^6$ $M^{-1}s^{-1}$ (1,1-diphenylethene) at 278 K, and the frequency factors are in the narrow range of $\log (A/M^{-1}s^{-1}) = 8.7 \pm 0.3$. $\cdot CH_2CO_2C(CH_3)_3$ shows a very similar reactivity with rate constants at 296 K ranging from $1.1 \cdot 10^4$ $M^{-1}s^{-1}$ (ethene) to 10^7 $M^{-1}s^{-1}$ (1,1-diphenylethene) and frequency factors $\log (A/M^{-1}s^{-1}) = 8.4 \pm 0.1$. For both radicals, the rate constants and the activation energies for addition to $CH_2{=}CXY$ correlate well with the overall reaction enthalpy. In contrast to the expectation of an electro- or ambiphilic behavior, polar alkene-substituent effects are not clearly expressed, but some deviations from the enthalpy correlations point to a weak electrophilicity of the radicals. The rate constants for the addition to 1,2- and to trisubstituted alkenes reveal additional steric substituent effects. Self-termination rate data for the title radicals and spectral properties of their adducts to the alkenes are also given.

1. Introduction. – The addition of carbon-centered radicals to C=C bonds is one of the most useful radical reactions. However, its rate constants are far from being quantitatively understood and predictable, because they reflect a complex interplay of polar, steric, and enthalpic substituent effects [1]. To provide a larger basis for their analysis, we have developed a technique of time-resolved electron spin resonance (ESR) which yields reliable rate data for large series of reactions with moderate efforts. Hitherto [2], the addition rates of the easily oxidizable radicals *tert*-butyl, hydroxymethyl, and 2-hydroxy-2-propyl to various alkenes $CH_2{=}CXY$ were found to correlate well with the alkene electron affinities. This means that these radicals are nucleophilic, and indicates a substantial stabilization of the transition state by partial electron transfer to the substrates. The variations of the reaction enthalpy had little or no effect. On the other hand, these were found to govern the rate constants for the addition of the 2-cyano-2-propyl radical [3] which exhibits no clear polar effects, and the benzyl radical shows an intermediate, weakly nucleophilic behavior [4]. In related studies, other groups demonstrated clearcut electrophilic reactivity patterns for perfluoroalkyl [5], dicyanomethyl [6], and malonyl [7] radicals.

Here, we present rate data for the addition of the cyanomethyl ($\cdot CH_2CN$) and the (*tert*-butoxy)carbonylmethyl ($\cdot CH_2CO_2C(CH_3)_3$) radical to various alkenes. These radicals are commonly considered as being about equally reactive and weakly electrophilic or ambiphilic [1] [8]. In the latter case, they react faster with both electron-deficient and electron-rich alkenes than with ethene because of favorable SOMO-HOMO and SOMO-

LUMO interactions which correspond to partial electron transfer to and from the radical, *i.e.*, polar effects in either direction. In fact, our previous interpretation of rate constants for the addition of the radical $\cdot CH_2CO_2C(CH_3)_3$ to several alkenes [9] supported this view. However, it ignored possible effects of the reaction enthalpy. Their importance for such borderline cases was found more recently by *Giese et al.* [8a] and is quite generally emphasized by *Radom* and coworkers [10] for all alkyl-radical additions on the basis of high-level *ab initio* calculations. Therefore, we now present a more comprehensive study of $\cdot CH_2CO_2C(CH_3)_3$, new data for $\cdot CH_2CN$ and a more complete analysis.

2. Methods and Results. – Our experimental arrangement and the procedures for steady-state and time-resolved ESR spectroscopy of photochemically generated transient free radicals in solution have amply been described in [2–4] [9]. Oxygen-free solutions of suitable radical precursors are photolyzed continuously or intermittent while flowing through a flat reaction cell in the ESR cavity and are thermostated by a surrounding N_2 stream. In kinetic experiments with intermittent photolysis, one of the center lines of $\cdot CH_2CN$ or $\cdot CH_2CO_2C(CH_3)_3$ was followed in time, and 100'000 to 200'000 individual signal *vs.* time profiles were accumulated to obtain a sufficient signal-to-noise ratio. The flow rates were adjusted so that the signal intensities did not depend on the dwell time of the solutions in the cell (0.83 to 6.3 ml/min). This ensures negligible substrate depletion. Rate constants were obtained by fitting the radical decay in the light-off period to $S(t) = S(0)\cdot\exp(-t/\tau_1)/(1 + t/\tau_2)$, where in the absence of side reactions $\tau_1 = (k\cdot[A])^{-1}$ is the pseudo-first-order life-time due to the addition of the radical to the alkene A, $\tau_2 = (2k_t\cdot[R(0)])^{-1}$ is the second-order life-time due to the self-termination, and $S(0)$ and $[R(0)]$ are the signal and the radical concentrations at the onset of the decay. Typical values were $0.4 \leqslant \tau_2 \leqslant 0.8$ ms and $\tau_1 > 1$ ms.

The radical $\cdot CH_2CN$ was produced by photolyzing CH_3CN (*Riedel-deHaen*) solutions containing 0.024M dibenzoyl peroxide (*Aldrich*, $\varepsilon \approx 1000$ $M^{-1}\cdot cm^{-1}$ at $\lambda \approx 280$ nm). In the absence of alkenes, it is the only observable radical species ($g = 2.0030$, $2H_a = 20.95$ G, $^{14}N = 3.48$ G at 278 K, see *Fig. 1a*), and is formed in the reaction sequence

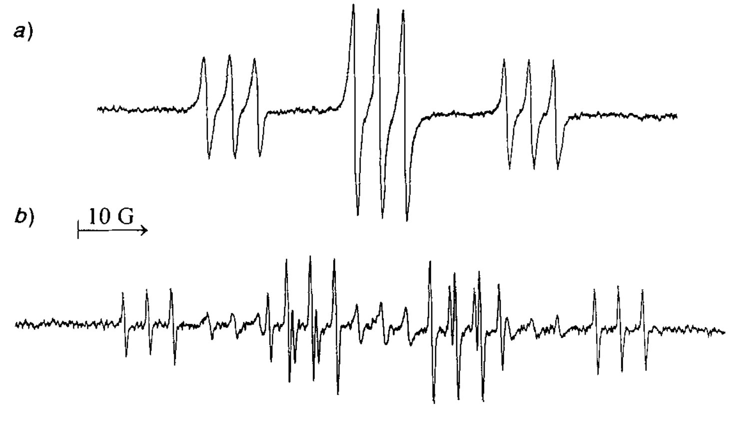

Fig. 1. *ESR Spectra obtained during photolysis of dibenzoyl peroxide in acetonitrile;* a) *in the absence of alkenes,* b) *in the presence of 0.03* M *acrylonitrile*

$$(C_6H_5CO_2)_2 \xrightarrow{h\nu} 2(1-f)\,C_6H_5COO\cdot + 2f C_6H_5 + 2f CO_2 \qquad (1)$$

$$C_6H_5COO\cdot \rightarrow \cdot C_6H_5 + CO_2 \qquad (2)$$

$$\cdot C_6H_5 + CH_3CN \rightarrow C_6H_6 + \cdot CH_2CN \qquad (3)$$

At room temperature the fraction of multibond cleavage is $f \approx 0.29$ [11], the benzoyl radical undergoes fragmentation (*Eqn. 2*) within *ca.* 200 ns [11], and the H abstraction (*Eqn. 3*) has a rate constant of *ca.* 10^5 $\text{M}^{-1}\text{s}^{-1}$ [12]. These fast processes are not resolved by our technique, and, hence, $\cdot CH_2CN$ is the only kinetically relevant radical species. This is confirmed by its pure second-order decay in the absence of alkenes which is ascribed to the self-termination

$$2\ \cdot CH_2CN \rightarrow NCCH_2CH_2CN\ (+\ CH_2{=}C{=}N{-}CH_2CN) \qquad (4)$$

The same was found in the full temperature range covered in this work, $250 \leqslant T \leqslant 300$ K. Using standard procedures and a calibration with $2k_t = 3.3 \cdot 10^9$ $\text{M}^{-1}\text{s}^{-1}$ for the *tert*-butyl self-termination in tetradecane at 298 K [13] the rate constants for *Reaction 4* were obtained. They are described by $\log(A/\text{M}^{-1}\text{s}^{-1}) = 11.8 \pm 0.5$ and $E_a = (10.5 \pm 2.8)$ kJ/mol, which agrees very well with literature data [14] and confirms that the self-termination is diffusion-controlled.

For the generation of $\cdot CH_2CO_2C(CH_3)_3$, we used the *Norrish* type-I cleavage of the corresponding disubstituted ketone (*Fluka*, recrystallized, $\varepsilon = 10$ $\text{M}^{-1}\text{s}^{-1}$ at $\lambda_{max} \approx 280$ nm) *ca.* 0.1 to 0.3M in CH_3CN solution.

$$((CH_3)_3CO_2CCH_2)_2CO \xrightarrow{h\nu} (CH_3)_3CO_2CCH_2\dot{C}O + \cdot CH_2CO_2C(CH_3)_3 \qquad (5)$$

$$(CH_3)_3CO_2CCH_2\dot{C}O \rightarrow \cdot CH_2CO_2C(CH_3)_3 + CO \qquad (6)$$

During continuous photolysis and $T \geqslant 0°$, only $\cdot CH_2CO_2C(CH_3)_3$ was observable ($g = 2.0034$, $2H_a = 21.30$ G at 296 K) so that the decarbonylation (*Eqn. 6*) must occur within 100 µs after the ketone cleavage (*Eqn. 5*). This was confirmed by time-resolved CIDNP and CIDEP experiments at 296 K which also showed that the rate of *Reaction 6* must be even larger than 10^5 s^{-1}, *i.e.*, it is faster than measurable. Kinetic traces obtained with alkene-free solutions exhibited a second-order decay perturbed by pseudo-first-order contributions. Variation of the ketone concentration and product analyses showed that these pseudo-first-order contributions are caused by H abstractions from the solvent and the parent ketone

$$\cdot CH_2CO_2C(CH_3)_3 + CH_3CN \rightarrow CH_3CO_2C(CH_3)_3 + \cdot CH_2CN \qquad (7)$$

$$\cdot CH_2CO_2C(CH_3)_3 + ((CH_3)_3CO_2CCH_2)_2CO \rightarrow CH_3CO_2C(CH_3)_3 + K\cdot \qquad (8)$$

where K· stands for a ketone-derived radical. The rate data are $\log(A/\text{M}^{-1}\text{s}^{-1}) = 6.8 \pm 0.1$, $E_a = (37.0 \pm 1.0)$ kJ/mol for *Reaction 7* and $\log(A/\text{M}^{-1}\text{s}^{-1}) = 8.0 \pm 0.8$, $E_a = (35.3 \pm 3.6)$ kJ/mol for *Reaction 8*. In determinations of the addition rate constants, they were used to correct the observed pseudo-first-order life-times *via* $\tau^{-1}_{1obs} = \tau^{-1}_{1add} + \tau^{-1}_{1abs}$. The self-termination rate constant of $\cdot CH_2CO_2C(CH_3)_3$ was also measured as $2k_t = (7.9 \pm 0.7) \cdot 10^9$ $\text{M}^{-1}\text{s}^{-1}$ at 295 K and is of the order of magnitude expected for diffusion control. The radicals $\cdot CH_2CO_2CH_3$ and $\cdot CH_2CO_2CH_2CH_3$ were likewise produced by photolysis of their ketone precursors and showed the same reactions in alkene-free solutions. Because they exhibit more and, therefore, weaker ESR lines than $\cdot CH_2CO_2C(CH_3)_3$, they were not applied in kinetic studies, however.

With alkenes added to the solutions, the ESR spectra of the primary radicals $\cdot CH_2CN$ and $\cdot CH_2CO_2C(CH_3)_3$ are partially replaced by those formed by addition. The latter were analyzed using continuous photolysis and rather high alkene concentrations ($\geqslant 10^{-2}$ M), and an example is given in *Fig. 1b*, where the alkene is acrylonitrile. In addition to the spectrum of $\cdot CH_2CN$ (*Fig. 1a*), one notices the spectral features of a radical of type $RCH_2\dot{C}HCN$ with one α-proton, two β-protons, and a CN group at the radical center, *i.e.*, very likely $NCCH_2CH_2\dot{C}HCN$. *Tables 1–3* give the g factors and the coupling constants of all adduct radicals identified in this work. They have the general structures expected for predominant addition to the least substituted alkene C-atom, and, for several additions, the nature of the adding radical is confirmed by the observation of

Table 1. g *Factors* (±0.0001) *and Coupling Constants* (±0.05 G) *of Adduct Radicals* $NCCH_2CH_2\dot{C}XY$ *from Alkenes* ($H_2C{=}CXY$) *in Acetonitrile*

X	Y	T [K]	g	H_α	$2\,H_\beta$	$3\,H_\beta$	Others
H	CN	274	2.0030	20.31	22.93	–	3.47 (^{14}N)
H	COOMe	295	2.0036	20.35	21.90	–	1.45 ($3\,H_\delta(OCH_3)$)
CH_3	CN	276	2.0027	–	19.40	20.88	3.38 (^{14}N)
CH_3	COOMe	295	–	–	13.92	22.10	1.30 ($3\,H_\delta(OCH_3)$)
Cl	Cl	278	2.0079	–	11.48	–	3.30 ($2\,^{35}Cl$)

Table 2. g *Factors* (±0.0001) *and Coupling Constants* (±0.1 G) *of Adduct Radicals* $(H_3C)_3CO_2CCH_2CH_2\dot{C}XY$ *from Alkenes* ($H_2C{=}CXY$) *in Acetonitrile*

X	Y	T [K]	g	H_α	$2\,H_\beta$	$3\,H_\beta$	$2\,H_\gamma$	Others
H	CN	325	2.0029	20.3	23.3	–	–	3.4 (^{14}N)
H	CF_3	299	2.0026	23.1	27.1	–	–	30.9 ($3\,^{19}F$)
H	$SiCl_3$	298	2.0025	20.7	25.1	–	–	–
H	$SiMe_3$	302	2.0027	20.1	24.6	–	–	0.4 ($9\,H_\gamma$)
H	$Si(OEt)_3$	293	2.0026	20.4	25.8	–	–	–
H	CH_2CN	297	2.0028	22.1	25.3/23.8[a])	–	–	–
H	C_2H_5	301	2.0027	21.4	25.3/24.3[a])	–	0.48	0.24 ($3\,H_\gamma$)
H	CMe_3	305	2.0026	21.3	27.2	–	–	0.6 ($9\,H_\gamma$)
H	CH_2SiMe_3	296	2.0029	20.7	24.4	–	–	18.4 ($2\,H_\beta(CH_2Si)$)
H	CO_2Me	304	2.0034	20.5	22.9	–	–	1.3 ($3\,H_\delta(OMe)$)
H	OEt	330	2.0032	14.0	18.7	–	0.5	1.5 ($2\,H_\gamma(OCH_2)$)
H	OCOMe	300	2.0028	18.9	21.5	–	0.6	1.3 ($3\,H_\delta(OMe)$)
H	$SCMe_3$	297	2.0043	16.7	16.7	–	–	–
Me	CN	299	2.0030	–	20.7	20.7	–	3.4 (^{14}N)
Me	CMe_3	329	2.0026	–	16.8	22.8	–	–
Me	CO_2Me	305	2.0034	–	15.8	22.0	–	1.3 ($3\,H_\delta(OMe)$)
Me	Cl	309	2.0053	–	12.7	22.7	–	2.0 (^{35}Cl)
Me	OMe	315	2.0031	–	15.6	20.3	0.7	1.5 ($3\,H_\gamma(OMe)$)
Me	OCOMe	303	2.0028	–	18.9	22.4	–	–
Cl	Cl	303	2.0077	–	11.7	–	–	3.3 ($2\,^{35}Cl$)

[a]) Magnetically inequivalent H-atoms.

Table 3. g *Factors* (±0.0001) *and Coupling Constants* (±0.1 G) *of Adduct Radicals* $(H_3C)_3CO_2CCH_2CHZ\dot{C}XY$ *from Alkenes* (HZC=CXY) *in Acetonitrile*

Z	X	Y	T[K]	g	H_α	H_β	Others
Me	H	CN[a])	298	2.0028	20.1	22.0	3.5 (^{14}N)
Me	Cl	Cl	299	–	–	8.5	4.2 (2 ^{35}Cl)
Cl	Cl	Cl	296	–	–	25.0	3.5 (2 ^{35}Cl), 3.8 (^{35}Cl)

[a]) (*E*)-Alkene.

γ-CH_2 splittings. For the styrenes, the spectra of the adduct radicals were not completely analyzed, because they contained to many overlapping sharp lines, but this also points to addition at the CH_2 C-atom. We have never found secondary radicals formed by addition at the more substituted C-atom or by H abstraction. The rate constants given below are hence assigned to a predominant if not exclusive addition at the less substituted alkene C-atom for all cases.

The rate constants for the addition of $\cdot CH_2CN$ and $\cdot CH_2CO_2C(CH_3)_3$ were determined from the pseudo-first-order life-times measured for different alkene concentrations, and *Fig. 2* shows two examples for the procedure. Plots of τ_t^{-1} *vs.* the alkene

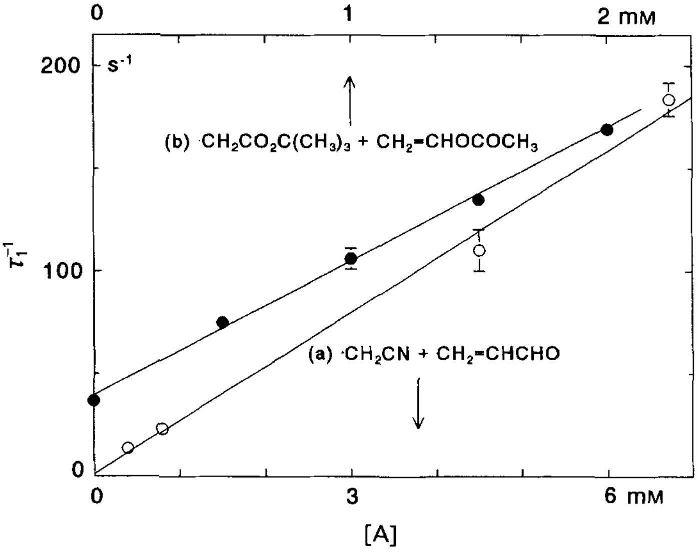

Fig. 2. *Pseudo-first-order plot for two radical addition reactions*

concentrations were linear which ensured the validity of the method and yielded k from the slopes. The non-zero value at $[A] = 0$ of τ_t^{-1} for $\cdot CH_2CO_2C(CH_3)_3$ is due to the reactions with ketone and solvent (*Eqns. 7* and *8*). Experiments at different temperatures then gave the *Arrhenius* parameters for the additions by fits of the *Arrhenius* expression to the data (*Fig. 3*). All results are presented in *Tables 4–6* where the alkenes are ordered

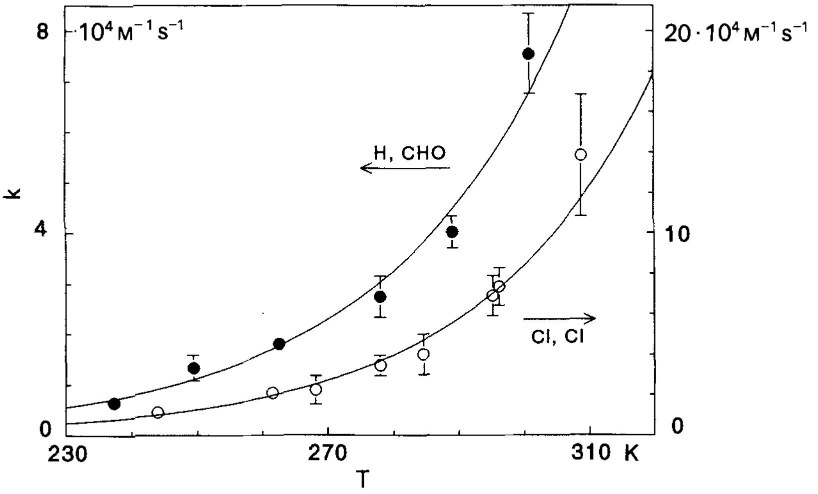

Fig. 3. *Temperature dependence of two addition rate constants of* $\cdot CH_2CN$ *and fits to the* Arrhenius *law*

Table 4. *Absolute Rate Constants*[a]) (at 278 ± 1 K), *Frequency Factor* A[a]), *and Activation Energy* E_a[a]) (Temperature Range 237–311 K) *for* $\dot{C}H_2CN$ *Radical Additions to Alkenes* ($H_2C{=}CXY$) *in Acetonitrile*

X	Y	*c* [mM]	*n*	k_{278} [10^3 $\mathrm{M}^{-1}\mathrm{s}^{-1}$]	log (A/$\mathrm{M}^{-1}\mathrm{s}^{-1}$)	E_a [kJ/mol]
H	H	21.1–58.9	10	3.3 (1)[b])	–	–
H	Et	9.6–58.3	6	11 (2)	–	–
Me	Me	5.7–13.3	16	11 (1)	–	–
H	Cl	10.0–15.5	8	12 (2)	–	–
H	Me	16.4–23.5	8	12 (1)	–	–
H	OCOMe	4.0–12.0	7	13 (3)	–	–
H	$SiMe_3$	6.0–14.0	45	13 (1)	8.4 (5)	24.1 (29)
Me	Cl	2.0–30.0	52	16 (2)	8.9 (3)	25.1 (16)
H	CHO	0.4–6.7	35	25 (3)	8.5 (3)	21.1 (17)
Cl	Cl	4.0–20.0	34	33 (2)	8.8 (5)	22.9 (29)
Me	OMe	2.0–8.0	27	35 (2)	8.9 (2)	23.2 (12)
H	OEt	4.0–6.0	7	43 (1)	–	–
Me	OCOMe	1.7–2.2	7	52 (2)	–	–
H	CO_2Me	2.4–10.0	8	110 (14)	–	–
H	CN	1.0–4.0	31	110 (10)	8.4 (7)	17.7 (48)
Me	CN	0.5–1.0	6	170 (10)	–	–
Me	CO_2Me	0.2–0.4	7	240 (10)	–	–
H	Ph	0.5–1.0	9	380 (10)	–	–
Me	Ph	0.2–0.38	7	660 (10)	–	–
Ph	Ph	0.15–0.3	6	2400 (100)	–	–

[a]) Standard deviation in units of the last digital number given in brackets.
[b]) Statistically corrected.

Table 5. *Absolute Rate Constants*[a]) (at 296 ± 1 K), *Frequency Factor* A[a]), *and Activation Energy* E_a[a]) (Temperature Range 295–330 K) *for* $\dot{C}H_2CO_2C(CH_3)_3$ *Radical Additions to Alkenes* ($H_2C{=}CXY$) *in Acetonitrile*

X	Y	*c* [mM]	*n*	k_{296} [10^3 M^{-1}s^{-1}]	log(*A*/M^{-1}s^{-1})	E_a [kJ/mol]
H	H	1.0–4.0	5	11 (2)[b])	–	–
H	CF_3	2 –10	28	15 (1)	8.4 (8)	24.0 (28)
H	CMe_3	1.0–3.1	19	35 (2)	8.5 (3)	22.1 (36)
H	CH_2CN	0.2–3.2	30	44 (4)	8.6 (3)	23.3 (29)
H	Et	0.4–1.5	29	54 (1)	7.9 (6)	26.5 (22)
H	OCOMe	0.5–2.0	30	65 (2)	8.1 (3)	18.5 (36)
H	$Si(OEt)_3$	0.5–3.0	28	67 (2)	7.6 (4)	16.2 (16)
H	Cl	0.5–2.5	31	71 (1)	8.4 (6)	20.1 (23)
H	Me	0.9–3.6	26	75 (5)	8.9 (3)	23.2 (40)
Me	OCOMe	0.3–1.5	27	88 (4)	9.1 (4)	23.5 (62)
H	$SiMe_3$	0.5–2.0	30	89 (3)	8.3 (4)	18.5 (49)
H	CH_2SiMe_3	0.5–1.5	30	95 (4)	8.5 (8)	19.1 (27)
Me	OMe	0.2–0.8	29	140 (10)	8.1 (4)	15.8 (52)
H	OEt	0.2–0.8	23	150 (3)	8.3 (4)	17.1 (46)
Me	Cl	0.2–1.5	26	160 (10)	8.4 (3)	17.7 (34)
Me	CMe_3	0.3–0.8	23	170 (5)	8.5 (7)	18.1 (26)
Me	Me	0.3–1.3	12	180 (8)	–	–
Cl	Cl	0.2–0.4	5	270 (10)	–	–
H	CHO	0.7–1.6	9	380 (10)	–	–
H	COOMe	0.1–0.2	6	490 (20)	–	–
H	CN	0.1–0.2	6	540 (50)	–	–
H	$SiCl_3$	0.05–0.2	6	870 (180)	–	–
Me	CN	0.05–0.2	11	910 (70)	–	–
H	$SCMe_3$	0.1–0.5	10	920 (150)	–	–
Me	COOMe	0.05–0.2	6	1300 (200)	–	–
H	SO_2Ph	0.05–0.5	19	1500 (200)	–	–
H	Ph	0.05–0.2	8	1900 (200)	–	–
Me	Ph	0.05–0.2	11	3900 (100)	–	–
Ph	Ph	0.1	1	≈ 10000	–	–

[a]) Standard deviation in units of the last digital number given in brackets.

[b]) Statistically corrected.

Table 6. *Absolute Rate Constants*[a]) (at 296 ± 1 K), *Frequency Factor* A[a]), *and Activation Energy* E_a[a]) (Temperature Range 295–330 K) *for* $\dot{C}H_2CO_2C(CH_3)_3$ *Radical Additions to Alkenes* ($HZC{=}CXY$) *in Acetonitrile*

Z	X	Y	*c* [mM]	*n*	k_{296} [10^3 M^{-1}s^{-1}]	log(*A*/M^{-1}s^{-1})	E_a [kJ/mol]
Cl	Cl	H[c])	10.0–50.0	23	0.8 (2)[b])	10.4 (4)[b])	44.2 (71)
Cl	Cl	H[d])	5.0–50.0	23	2.4 (2)[b])	8.2 (3)[b])	27.2 (31)
Cl	Cl	Cl	1.0–10.0	28	12 (1)	6.4 (4)	13.1 (45)
Me	CN	H[d])	1.0–5.0	24	14 (1)	9.1 (4)	27.4 (51)
Me	Cl	Cl	1.0–5.0	25	32 (5)	9.1 (2)	25.7 (60)

[a]) Standard deviation in units of the last digital number given in brackets.

[b]) Statistically corrected.

[c]) (*Z*)-Alkene.

[d]) (*E*)-Alkene.

according to increasing reactivities. We also list the ranges of alkene concentrations employed and the number of kinetic experiments evaluated for determination of the activation parameters. For both radicals, the observed frequency factors of addition to mono- and 1,1-disubstituted alkenes $CH_2{=}CXY$ are in the narrow ranges of log (A/$M^{-1}s^{-1}$) = 8.7 ± 0.3 for $\cdot CH_2CN$ and log (A/$M^{-1}s^{-1}$) = 8.4 ± 0.1 for $\cdot CH_2CO_2C(CH_3)_3$, respectively. Similar narrow ranges have previously been found also for the *tert*-butyl, for the hydroxymethyl radical, and for the benzyl radical [2] [4], though with other values. This suggests that the above ranges also hold for those alkenes $CH_2{=}CXY$ for which the temperature dependence was not measured, *i.e.*, the variation of the rate constants with substitution of these alkenes is ascribed to variations of the activation energy, only. The frequency factors for the 1,2-di- and trisubstituted alkenes (*Table 6*) are different.

As far as we know, there are no directly measured absolute rate constants from other sources with which our results could be compared. By an indirect telomerization technique, *Myshkin et al.* [15] derived $k_{453} = 280$ $M^{-1}s^{-1}$ for the addition of $\cdot CH_2CO_2H$ to ethene which we believe to be at least two orders of magnitude too low. However, several relative rate data confirm our reactivity ratios. From product distributions in additions of $\cdot CH_2CN$ and $\cdot CH_2CO_2CH_2CH_3$ to pairs of α-substituted styrenes and unsaturated heterocyclic compounds, *Giese et al.* [8a] and *Baciocchi et al.* [8b] deduced that the selectivities of the two radicals are very similar, and the same was observed by *Newcomb et al.* [8c] for a 5-*exo*-radical cyclization. This similarity is emphasized here by a plot of log ($k_{296}(\cdot CH_2CO_2C(CH_3)_3)$/$M^{-1}s^{-1}$) *vs.* log ($k_{278}(\cdot CH_2CN)$/$M^{-1}s^{-1}$) for the 20 alkenes for which both values are available from *Tables 4* and *5* (*Fig. 4*). Five cases may be affected by experimental errors, but there is an excellent correlation of log ($k_{296}(\cdot CH_2CO_2C(CH_3)_3)$/

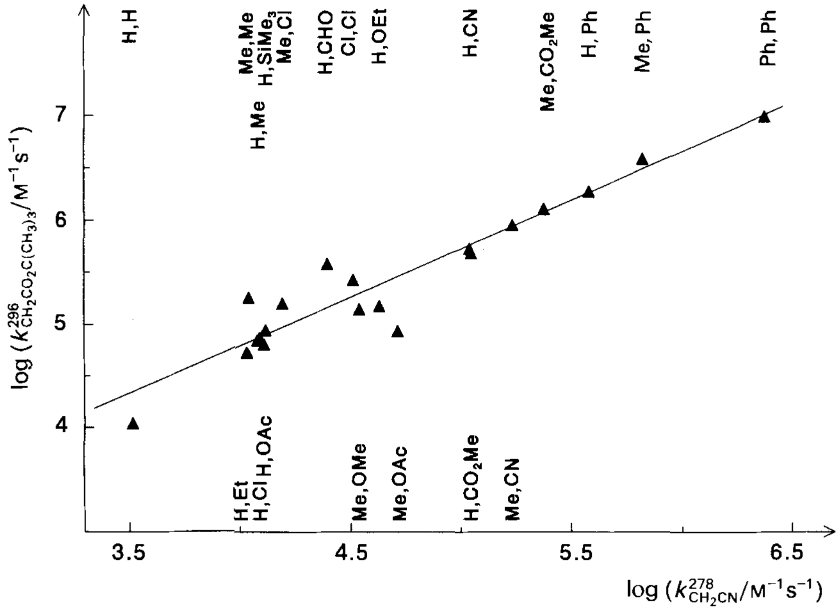

Fig. 4. *Correlation of the addition rate constants of $\cdot CH_2CO_2C(CH_3)_3$ and $\cdot CH_2CN$*

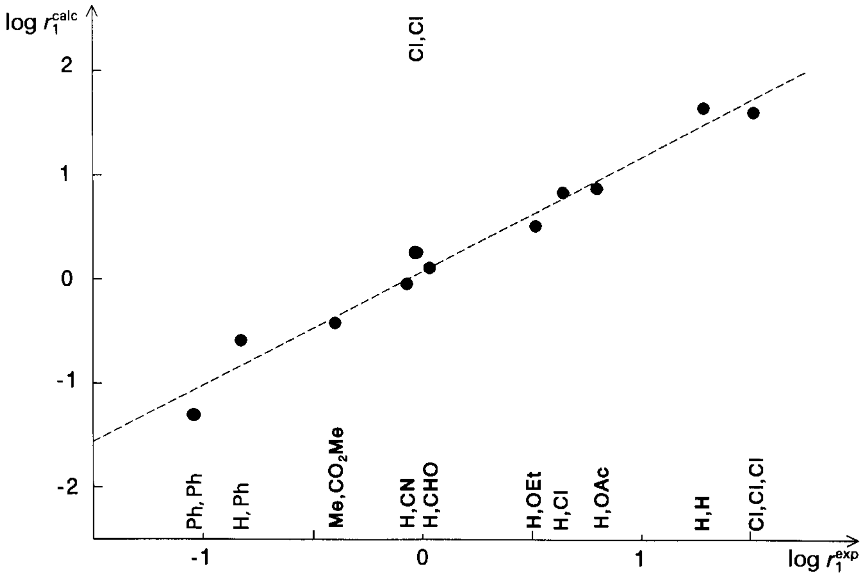

Fig. 5. *Correlation of relative rate constants for the addition of* $\cdot CH_2CO_2C(CH_3)_3$ *to alkenes with the copolymerization parameter* r_1 *of methylacrylate*

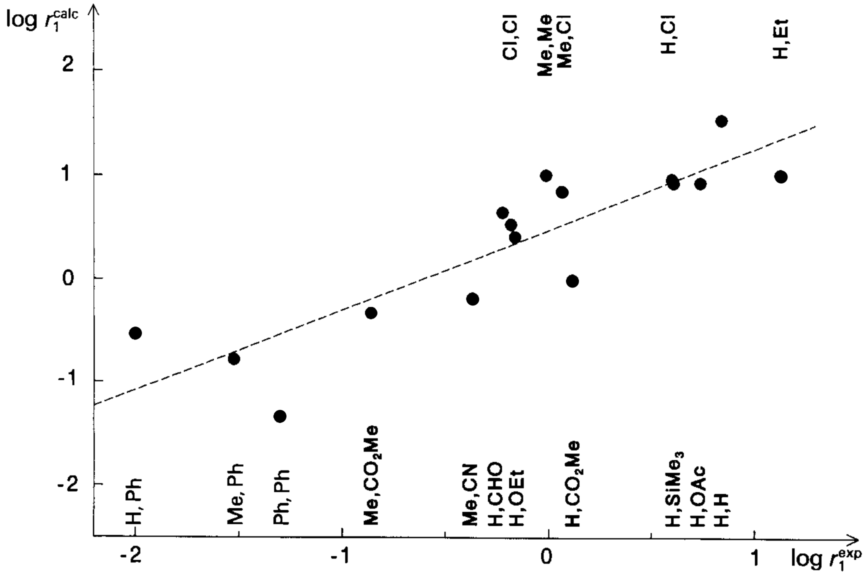

Fig. 6. *Correlation of relative rate constants for the addition of* $\cdot CH_2CN$ *to alkenes with the copolymerization parameter* r_1 *of acrylonitrile*

$\mathrm{M}^{-1}\mathrm{s}^{-1}) = 1.0501 + 0.9349 \cdot \log (k_{278}(\cdot \mathrm{CH_2CN})/\mathrm{M}^{-1}\mathrm{s}^{-1})$, $r = 0.952$, 20 points. Obviously, the reactivity of both radicals depends in the same way on the substitution of the alkene, *i.e.*, they do have very similar selectivities. The average ratio obeys $k_{296}(\cdot \mathrm{CH_2CO_2C(CH_3)_3})/k_{278}(\cdot \mathrm{CH_2CN}) = 5.00 \pm 0.97$, the carboxy-substituted radical being more reactive. Also, our trends of substituent effects are similar to those observed by *Giese et al.* [8a]. Furthermore, they parallel those of the copolymerization parameters r_1 of methylacrylate and acrylonitrile which are the rate constants for addition of the two propagating radicals ($\sim \mathrm{CH_2\dot{C}HCO_2CH_3}$ and $\sim \mathrm{CH_2\dot{C}HCN}$) to their parent alkenes in relation to the rate constants for addition to other alkenes. *Figs. 5* and *6* show the correlations. The values of r_1^{exp} were taken from the standard compilation [16], and the most recent parameter was chosen, if more than one value is given. r_1^{calc} are the corresponding ratios derived from our data of *Tables 4* and *5*. In both *Figures* the slopes are close to unity, and the scatter in *Fig. 6* is likely due to uncertain copolymerization parameters [16].

3. Analysis and Discussion. – The ESR data of the parent and the adduct radicals (*Tables 1–3*) agree well with those known from the abundant literature on the same or similar species [17] and deserve no further comment. In the analysis of the rate constants, we first consider the additions to the 20 mono- and 1,1-disubstituted alkenes for which both radicals were investigated (*Tables 4* and *5*), and comment on the other data later.

Firstly, the additions occur highly regiospecifically to the unsubstituted C-atoms. This is attributed to steric effects of the substituents as usual [1] [2], and is also supported by additional data in this work (*vide infra*).

Secondly, the average frequency factors $\log (A/\mathrm{M}^{-1}\mathrm{s}^{-1}) = 8.7 \pm 0.3$ for $\cdot\mathrm{CH_2CN}$ and $\log (A/\mathrm{M}^{-1}\mathrm{s}^{-1}) = 8.4 \pm 0.1$ for $\cdot\mathrm{CH_2CO_2C(CH_3)_3}$ are close to the corresponding values for the additions of the two previously studied primary radicals hydroxymethyl (8.1 ± 0.1 [2c]) and benzyl (8.9 ± 1.0 [4]) to the same alkenes. This indicates rather similar transition-state structures, as they are also inferred from theoretical work [10] [18]: 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 newly linked C-atoms. Moreover, as was already pointed out earlier [2c], the increase of the frequency factors in the series $\cdot\mathrm{CH_2OH} < \cdot\mathrm{CH_2CO_2C(CH_3)_3} < \cdot\mathrm{CH_2CN} <$ benzyl may be significant. Since the exothermicity of the addition decreases in this order, the new C–C bond length in the transition state decreases [10], and the radical deformations should thus increase. Further, the four radicals possess partial $\mathrm{C}(\alpha),\mathrm{C}(\beta)$ double bonds which hinder their rotational and vibrational degrees of freedom, and the strength of the double bond increases in the series. In the transition state, the partial double-bond character is diminished, and, hence, the increasing frequency factors may reflect the correspondingly increasing gains in motional entropy which lower the overall loss to some extent.

The further major points of discussion are then the influences of the substituents X,Y of the alkenes $\mathrm{CH_2{=}CXY}$ on the rates and activation energies. These are usually ascribed either to changes of the total reaction enthalpy which reflect different stabilizations of the alkenes and the adduct radicals and/or a partial charge transfer, *i.e.*, polar effects in the transition state. Both effects can be visualized in a state correlation diagram [3] [10] [19] as presented schematically in *Fig. 7*. The activation barrier is described by the interaction of four electronic configurations, namely firstly an unpolar ground state which (in the

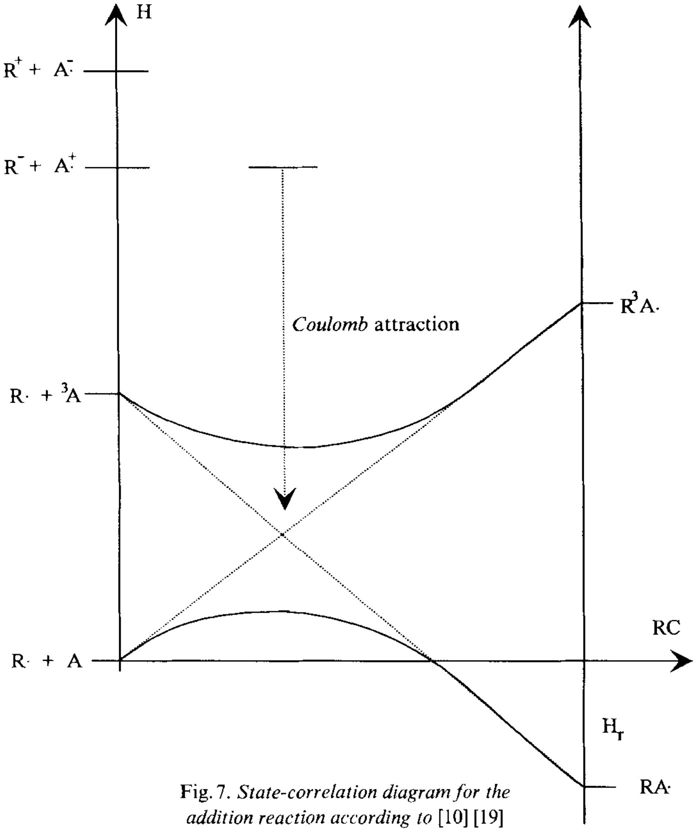

Fig. 7. *State-correlation diagram for the addition reaction according to* [10] [19]

hypothetical absence of the interactions) extrapolates on one side to the ground state $R\cdot + A$ of the separated radical $\cdot R$ and alkene A, and on the other to a locally excited triplet state of the new bond in the adduct radical, secondly an unpolar excited state which extrapolates to $R\cdot + {}^3A$, *i.e.*, the radical ground and the lowest alkene triplet state and to the ground state of the adduct radical, and in addition to two polar states which extrapolate to the charge-transfer states $R^+ + A^{-\cdot}$ and $R^- + A^{+\cdot}$ of the separated and the combined educts. If the polar states are unimportant, the barrier should be influenced mainly by the reaction enthalpy H_r, since the excitation energy of $R\cdot + A$ to $R\cdot + {}^3A$ (E_T) often parallels this quantity (see below), and since the local excitation energy of the adduct radical is unlikely to vary with the distant substituents. For the separated reactants, the energies of the polar states are given by $IP(\cdot R) - EA(A)$ and $IP(A) - EA(\cdot R)$, where IP and EA are the ionization potentials and electron affinities, respectively. These energies are high, but they are substantially lowered in the transition state by the *Coulomb* attraction. Within the frontier-orbital model, the contributions of the polar states correspond to SOMO-LUMO and SOMO-HOMO interactions of radical and alkene. Guided by these considerations, we now seek correlations of our kinetic data with the reaction enthalpies and the alkene electron affinities (EA) or ionization potentials (IP) as in other work [2–4] [9] [10]. We remark in passing that the polar effects can as well be judged by using polar substituent constants as basis for the analysis [1], because these correlate well with *EA* and/or *IP*. Since the activation energies were not measured for all cases, they were rederived as E_a^{res} from the rate constants of *Tables 4* and *5* using the average frequency factors given above.

Table 7 displays the energy quantities needed for the analysis of the data for the 20 common alkenes. The *IP* and *EA* values were taken from [20] and from sources cited in our earlier work [2–4] [9]. The estimation of the reaction enthalpy follows [2c] [3] and considers the reaction sequence

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

from which the reaction enthalpy for the radical-addition step can be expressed in terms of heats of formation h_f of stable compounds and bond dissociation energies *BDE*.

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

where A stands for the alkene. Since h_f(RAH) and *BDE*(RA–H) are known for many compounds with R = CH_3 but not for R = CH_2CN and $CH_2CO_2C(CH_3)_3$, we use here the values of H_r determined earlier [2c] for additions of the methyl radical to the same 20 alkenes and then increment for the substitution *via*

$$\begin{aligned} H_r(\cdot\mathrm{R}) = H_r(\cdot\mathrm{CH_3}) + h_f(\mathrm{RAH}) - h_f(\mathrm{CH_3AH}) - h_f(\mathrm{RH}) + h_f(\mathrm{CH_4}) \\ - BDE(\mathrm{R{-}H}) + BDE(\mathrm{CH_3{-}H}) \end{aligned} \quad (11)$$

assuming that *BDE*(RA–H) is not influenced by the change of R. In particular, in *Eqn. 11* the following data were used: for ·R = ·CH_2CN, *BDE*(R–H) = 393.5 kJ/mol [21] and h_f(RH) = 74 kJ/mol [22], for ·R = ·$CH_2CO_2C(CH_3)_3$, *BDE*(R–H) = 398 kJ/mol [23] and h_f(RH) = −510 kJ/mol [24], and for ·R = ·CH_3, *BDE*(R–H) = 436 kJ/mol [21] and h_f(RH) = −74.5 kJ/mol [20]. The difference h_f(RAH) − h_f(CH_3AH) was deduced from pairs of compounds found in [20] as +135.5 kJ/mol for R = CH_2CN and −448 kJ/mol for R = $CH_2CO_2C(CH_3)_3$. With these energies, the additions of ·CH_2CN and ·$CH_2CO_2C(CH_3)_3$ are 29.5 kJ/mol and 26 kJ/mol less exothermic than those of the methyl radical. Of course, this estimation of reaction enthalpies may be subject to considerable error, because we use gas-phase data and neglect solvent effects, and because the experimental bond-dissociation energies are known only with 5–10 kJ/mol accuracies. However, the enthalpy ordering of the substituents in *Table 7* and the only slightly lower exothermicity of the cyanomethyl compared to the carboxy-substituted radical agree with the common views of substituent effects on radical stabilization [25].

To investigate the influence of the reaction enthalpy on log *k* and E_a^{res}, these are plotted *vs.* H_r for both radicals in *Figs. 8* and *9*. Obviously, there are very good correlations, and linear regressions gave

$$\log (k_{278}/\mathrm{M^{-1}s^{-1}}) = (1.26 \pm 0.32) - (0.039 \pm 0.004)\cdot H_r\,[\mathrm{kJ/mol}] \quad (12)$$
$$r = 0.931$$

$$E_a^{res}\,[\mathrm{kJ/mol}] = (39.5 \pm 1.7) + (0.210 \pm 0.019)\cdot H_r\,[\mathrm{kJ/mol}] \quad (13)$$
$$r = 0.931$$

for ·CH_2CN, and

Table 7. *Energy Quantities for Radical Addition to Alkenes* ($H_2C{=}CXY$).
H_r, E_a^{res} in kJ/mol, *EA*, *IP* in eV[a]).

Alkenes				$\dot{C}H_2CN$		$\dot{C}H_2CO_2C(CH_3)_3$	
X	Y	*EA*	*IP*	H_r	E_a^{res}	H_r	E_a^{res}
Me	Cl	−1.44	9.76	−66.5	23.8	−70	18.1
H	OCOMe	−1.19	9.19	−67.5	24.3	−71	20.3
H	H	−1.78	10.51	−68.5	27.4	−72	24.7
Me	Me	−2.19	9.6	−70.5	24.6	−74	17.8
H	$SiMe_3$	−1.14	9.5	−72.5	24.2	−76	19.6
H	Et	−1.90	9.59	−74.5	24.7	−78	20.8
H	Me	−1.99	9.5	−74.5	24.4	−78	20.0
H	Cl	−1.28	10.0	−76.5	24.4	−80	20.1
H	OEt	−2.24	8.8	−76.5	21.5	−80	18.3
Me	OMe	−2.48	8.64	−79.5	22.0	−83	18.4
Me	OCOMe	−1.51	9.1	−87.5	21.0	−91	19.6
H	CHO	+0.03	10.1	−88.5	22.7	−92	16.0
H	COOMe	−0.49	9.9	−88.5	19.3	−92	15.4
Cl	Cl	−0.76	9.79	−89.5	22.1	−93	16.8
Me	CN	−0.17	10.35	−97.5	18.3	−101	13.8
Me	COOMe	−0.38	9.7	−100.5	17.5	−104	13.0
H	CN	−0.21	10.95	−109.5	19.3	−113	15.1
Me	Ph	−0.23	8.19	−109.5	15.2	−113	10.3
H	Ph	−0.25	8.43	−113.5	16.4	−117	12.0
Ph	Ph	+0.36	8.0	−123.5	12.2	−127	7.9

[a]) From [20] and previous works [2–4] [9].

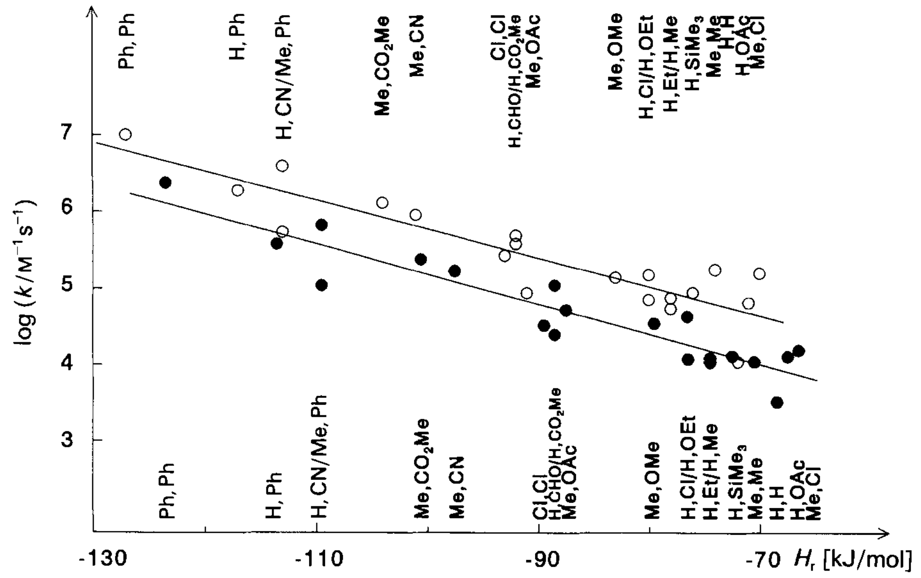

Fig. 8. *Rate constants for the addition of* $\cdot CH_2CO_2C(CH_3)_3$ (open circles) *and* $\cdot CH_2CN$ (full circles) *to mono- and 1,1-disubstituted alkenes* vs. *the reaction enthalpies*

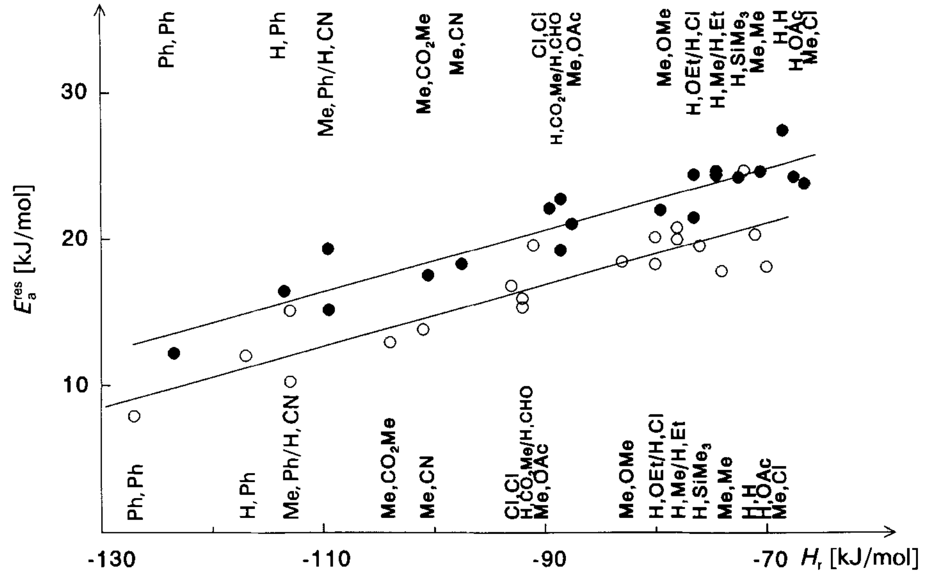

Fig. 9. *Activation energies for the addition of* $\cdot CH_2CO_2C(CH_3)_3$ (open circles) *and* $\cdot CH_2CN$ (full circles) *to mono- and 1,1-disubstituted alkenes* vs. *the reaction enthalpies*

$$\log (k_{296}/\mathrm{M}^{-1}\mathrm{s}^{-1}) = (2.07 \pm 0.40) - (0.037 \pm 0.004) \cdot H_r\ [\mathrm{kJ/mol}] \qquad (14)$$
$$r = 0.894$$

$$E_a^{res}\ [\mathrm{kJ/mol}] = (35.9 \pm 2.3) + (0.210 \pm 0.025) \cdot H_r\ [\mathrm{kJ/mol}] \qquad (15)$$
$$r = 0.894$$

for $\cdot CH_2CO_2C(CH_3)_3$. The slopes of the lines are practically identical in both *Figures*, and the H_r-independent terms reflect the lower average reactivity of cyanomethyl. Interestingly, previously published rate constants for the addition of the 2-cyano-2-propyl radical [3] to 16 alkenes, which belong to the present series of 20, gave correlations with very similar slopes.

$$\log (k_{315}/\mathrm{M}^{-1}\mathrm{s}^{-1}) = -(0.00 \pm 0.30) - (0.039 \pm 0.004) \cdot H_r\ [\mathrm{kJ/mol}] \qquad (16)$$
$$r = 0.922$$

$$E_a^{res}\ [\mathrm{kJ/mol}] = (46.5 \pm 1.8) + (0.238 \pm 0.027) \cdot H_r\ [\mathrm{kJ/mol}] \qquad (17)$$
$$r = 0.922$$

As a test for polar effects, *Figs. 10* and *11* show plots of log *k vs.* the alkene electron affinities and ionization potentials. The previously stated U-shape behavior [9] is confirmed, and for $\cdot CH_2CO_2C(CH_3)_3$ it is even more pronounced, if all alkenes of *Table 5* are included. This was taken as evidence for an ambiphilic reactivity. However, it is evident that the upward curvature in *Figs. 10* and *11* is caused by alkenes for which the exothermicity of the addition is also high, *i.e.*, by the styrenes, the acrylates, and the acrylonitriles. If these are omitted a very weak decrease of log *k* with increasing *IP* remains in *Fig. 11*, whereas the correlation with *EA* in *Fig. 10* vanishes.

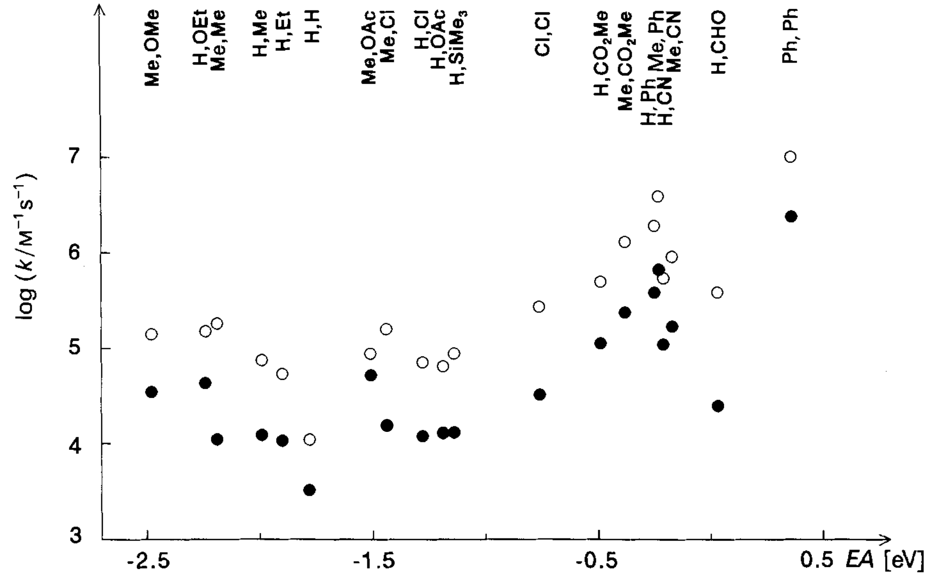

Fig. 10. *Rate constants for the addition of* $\cdot CH_2CO_2C(CH_3)_3$ (open circles) *and* $\cdot CH_2CN$ (full circles) *to mono- and 1,1-disubstituted alkenes* vs. *the electron affinities*

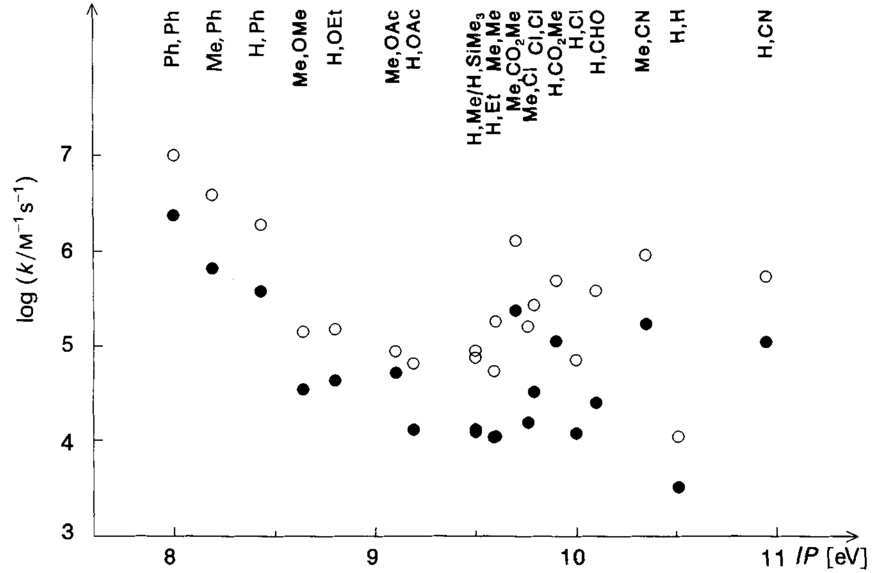

Fig. 11. *Rate constants for the addition of* $\cdot CH_2CO_2C(CH_3)_3$ (open circles) *and* $\cdot CH_2CN$ (full circles) *to mono- and 1,1-disubstituted alkenes* vs. *the ionization potentials*

At first glance, the good correlations of *Figs. 8* and *9* and the scatter in *Figs. 10* and *11* suggest a dominating influence of the reaction enthalpy and only minor polar effects. Yet, such an interpretation can be misleading, because the omission of the alkenes with high electron affinities from *Fig. 8* (styrenes, acrylates, acrylonitriles) and low ionization potentials from *Fig. 9* (styrenes), *i.e.*, alkenes which should reveal strong polar effects, considerably deteriorates the correlations with H_r. Hence, additional arguments are needed, and we turn to a closer discussion of the predictions from the state-correlation diagram.

If there are no polar contributions, the energy of the transition state is determined by the interaction of the states $R\cdot + A$ with $R\cdot + {}^3A$ only, which leads to an avoided crossing. The location of the hypothetical non-avoided crossing of these states can be fixed approximately, if H_r, the alkene triplet energy E_T, and the energy for local $\sigma\sigma^*$-triplet excitation of the new bond of the adduct radical are available. For six of our alkenes, namely ethene, 1,1-dimethyl- and 1,1-dichloroethene, and the styrenes, the lowest triplet energies are known [26]. They correlate well with our estimated reaction enthalpies, and for instance, $E_T = 465 + 1.751 \cdot H_r$ [kJ/mol] ($r = 0.978$), with H_r for the addition of $\cdot CH_2CN$. This means that the substituents stabilize the alkene triplets and the adduct radicals in a similar sense. The $\sigma\sigma^*$-triplet excitation energy of the new bond is not known but is expected to be *ca.* 5–6 eV and should not depend strongly on the substituents of the alkene. Assuming 5 eV for this quantity and a linear dependence of the state energies on a suitable reaction coordinate, the energy of the crossing is obtained for the six alkenes as $E_C = 239.8 + 0.9340 \cdot H_r$ [kJ/mol] ($r = 0.990$). It varies from 178 kJ/mol for ethene to 127 kJ/mol for 1,1-diphenylethene and the addition of $\cdot CH_2CN$ and similarly for the other radical. If the interaction of $R\cdot + A$ with $R\cdot + {}^3A$ were equal for all substituents, the correlation of the barrier E_a with H_r should also show the slope +0.9340. This cannot be expected, however, since lower exothermicities mean later transition states and larger molecular distortions which lead to larger energy gaps. Hence, the actual slopes of the E_a *vs.* H_r correlations should be smaller than +0.9340, and this is as observed.

On the other hand, marked polar contributions are expected, when the *Coulomb* attraction in the transition state lowers the energies of the charge-transfer states to or below the energies of the non-avoided crossing. In the latter case, the polar effects can override the influence of the reaction enthalpy. To estimate the relevant quantities, we use a *Coulomb* attraction of 6 eV [3] [10], the alkene data of *Table 7*, and $EA = 1.56$ eV [20] and $IP = 10.87$ eV [27] for $\cdot CH_2CN$, and $EA = 1.80$ eV [20] for $\cdot CH_2CO_2C(CH_3)_3$ (the value for $\cdot CH_2CO_2CH_3$). The unknown IP of $\cdot CH_2CO_2C(CH_3)_3$ is probably also *ca.* 10.0–10.5 eV. With these parameters, the polar configuration $R^+ + A^{-\cdot}$ lies at least 500 kJ/mol above the educt ground state for both radicals, *i.e.*, markedly above the crossing. This renders any contribution of a partial nucleophilicity of the radicals very unlikely, and, therefore, the increase of log k with increasing EA in *Fig. 10* is deceiving and must in fact be ascribed to the exothermicities of the corresponding additions. On the other hand, the state $R^- + A^{+\cdot}$, which represents electrophilic contributions, falls in or even below the crossing region, if the alkene IP is smaller than *ca.* 9.3 eV for $\cdot CH_2CN$ and smaller than *ca.* 9.5 eV for $\cdot CH_2CO_2C(CH_3)_3$. Therefore, polar effects of a partial charge transfer from the alkenes to the radicals are expected for the styrenes, the vinyl ethers and possibly also for the vinyl acetates in decreasing amounts. As *Fig. 11* shows, the rate constants obtained for these alkenes do in fact increase with decreasing IP. However, those of the ethers and the acetates are lower than those of many other compounds with higher *IP*, especially of the alkenes with large negative reaction enthalpies. Hence, at least the rate constants of the latter must be dominated by the reaction enthalpy. This view is also supported by the fact that omission of only the styrenes and the ethers from *Figs. 8* and *9* does not change the qualitative correlations. Yet, we think that the addition is not solely enthalpy-controlled, but that both radicals are slightly electrophilic and base this on specific substituent effects.

Fig. 12 shows $\Delta\log(k/\mathrm{M}^{-1}\mathrm{s}^{-1})$ for the three radicals $\cdot CH_2CN$, $\cdot CH_2CO_2C(CH_3)_3$, and 2-cyano-2-propyl corrected for the enthalpy-dependent terms of *Eqns. 12*, *14*, and *16*, and with the alkenes ordered according to increasing exothermicity of the additions. As pointed out before (*Fig. 4*), $\cdot CH_2CN$ and $\cdot CH_2CO_2C(CH_3)_3$ exhibit very similar substituent effects. Hence, the apparent scatter in *Figs. 8–11* is not statistical nor is it dominated by experimental errors. The 2-cyano-2-propyl radical follows the same trends though with differences in detail. Now, some major excursions from the means (arrows in *Fig. 12*) can easily be attributed to polar effects: The 2-cyano-2-propyl radical has a low

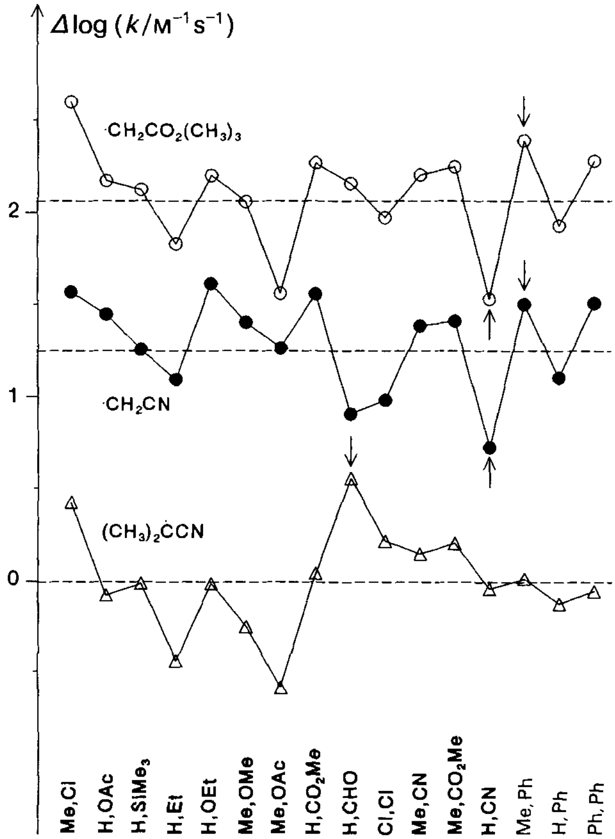

Fig. 12. *Deviations of the rate constants for the addition of* $\cdot CH_2CO_2C(CH_3)_3$ (open circles), $\cdot CH_2CN$ (full circles), *and* $(CH_3)_2\dot{C}CN$ (triangles) *from* Eqns. 12, 14, *and* 16 *to mono- and 1,1-disubstituted alkenes*

ionization potential of 8.2 eV [3] and should be slightly nucleophilic, therefore. This can explain the exceptionally high reactivity towards acrolein which has a very high electron affinity. Then, $\cdot CH_2CN$ and $\cdot CH_2CO_2C(CH_3)_3$ react remarkably faster with α-methylstyrene than with styrene. This is in contrast to all other radicals which we have studied so far [2–4], and which all have smaller electron affinities. It disagrees with an *EA* or an enthalpy correlation but agrees well with the ordering expected for electrophilic behavior, *i.e.*, the low *IP*. In the opposite sense, the unusually low reactivities towards acrylonitrile can be rationalized in terms of the very high alkene *IP* which excludes the electrophilic polar rate enhancement. Finally, the higher reactivity of $\cdot CH_2CO_2C(CH_3)_3$ in comparison with $\cdot CH_2CN$ can also be ascribed to a generally higher polar effect, because the former radical has the higher electron affinity. Of course, the reactivity difference could also be simply due to a smaller stabilization of $\cdot CH_2CO_2C(CH_3)_3$ and/or a larger one for $\cdot CH_2CN$, and an additional difference in H_r of 16 kJ/mol would suffice to have the lines in *Figs. 8* and *9* coincide. In view of the errors of the experimental bond dissociation energies used for the estimations, this seems unlikely, however.

Apart from the 20 rate constants and *Arrhenius* parameters analyzed so far, *Tables 5* and *6* contain data for the addition of $\cdot CH_2CO_2C(CH_3)_3$ to nine further mono- and 1,1-disubstituted, to three 1,2- disubstituted, and to two trisubstituted alkenes. Of these, we consider now three additional monosubstituted, and the 1,2-di- and trisubstituted species. The remaining alkenes are not discussed, because their substituents and rate constants are rather similar to similarly substituted ones, or because the reaction enthalpies could not be estimated with confidence. *Table 8* gives details on the estimation of the reaction enthalpies, the ionization potentials of the alkenes and comparisons of experimental values of log k_{296} with predictions from the log k/H_r correlation *via Eqn. 15*. Obviously, for two monosubstituted alkenes, *Eqn. 15* predicts the observed rate constants quite well which lends further credit to the enthalpy dominance. For $CH_2{=}CHCF_3$, the observed rate constant is lower than predicted. As for acrylonitrile, this is again understandable, if the general pattern is modulated by electrophilic polar rate enhancements. They should not occur for this alkene, because it also has a very high *IP*.

For the 1,2-disubstituted and the trisubstituted alkenes, the experimental rate constants are much lower than predicted, and this is quite obviously due to the well known retarding effect of alkene substituents at the site of addition [1] [2] which also explains the regioselectivity. In comparison with the predicted rates, the Cl substitution at the addition site decreases log *k* by an average 2.2 ± 0.3, and the Me substitution yields a decrease of 1.4 ± 0.4. These values agree with decreases of log *k* of 1.5 ± 0.3 and 1.3 ± 0.2, respectively, which were obtained for the addition of the *tert*-butyl radical in our earlier work [2].

Recently, *Radom* and coworkers [10] have presented *ab initio* studies of radical-alkene addition reactions on the high QCISD/6-311** + ZPVE level which are the most comprehensive and deepest theoretical investigations currently available. They studied the radicals methyl, hydroxymethyl, cyanomethyl, and *tert*-butyl, and the common six alkenes $CH_2{=}CHX$ where X = H, F, Cl, NH_2, CHO, and CN. The authors also relate the calculated barrier heights for these six alkenes to calculated reaction enthalpies, electron affinities, and ionization potentials, and derive conclusions with the aid of the state-correlation diagram as we do above. It is clear that the theoretical data refer to gas-phase reactions. Therefore, the following comparison with our findings can be ambiguous, since

Table 8. *Energy Quantities and Comparisons of Experimental and Calculated Rate Constants for the Addition of* $\dot{C}H_2CO_2C(CH_3)_3$ *to Several Alkenes*

Alkene	h_f a) (A)	h_f a) (CH_3AH)	*BDE* a) ($CH_3A{-}H$)	H_r a)	*IP* a)	$\log k^{exp}$	$\log k^{calc}$
$H_2C{=}CHCF_3$	−614 b)	−792 c)	430 d)	−84	10.9 b)	4.2	5.1 ± 0.8
$H_2C{=}CHSCMe_3$	−13 e)	−167 f)	373 g)	−117	8.1 h)	6.0	6.4 ± 0.9
$H_2C{=}CHSO_2Ph$	−133 i)	−296 i)	395 k)	−104	10.4 l)	6.2	6.0 ± 0.9
(*Z*)-$ClHC{=}CHCl$	4 b)	−163 b)	411 m)	−92	9.6 b)	2.9	5.4 ± 0.8
(*E*)-$ClHC{=}CHCl$	6 b)	−163 b)	411 m)	−94	9.6 b)	3.4	5.5 ± 0.8
$ClHC{=}CCl_2$	−16 n)	−182 o)	394 m)	−108	9.5 p)	4.1	6.0 ± 0.9
$MeHC{=}CCl_2$	−30 q)	−182 r)	394 m)	−94	9.4 l)	4.5	5.5 ± 0.8
(*E*)-$MeHC{=}CCN$	150 b)	4 s)	376 t)	−106	10.2 b)	4.2	6.0 ± 0.9

a) Enthalpies in kJ/mol, *IP* in eV, *k* in $M^{-1}s^{-1}$ at 296 K.

b) From [19].

c) From $h_f(CH_3CF_3) = -749$ kJ/mol and $\Delta h_f(CH_3CH_2CH_2CH_3/CH_3CH_3) = -42.5$ kJ/mol [19].

d) From $BDE(CF_3CH_2{-}H) = 446$ kJ/mol [28] and $\Delta BDE(CH_3CH_2CH_2{-}H/CH_3CH_2CH(CH_3){-}H) = 16$ kJ/mol [20].

e) From $h_f(CH_2{=}CHSCH_3) = 74$ kJ/mol [19] and *Benson* group increments.

f) From $h_f(CH_3SCH_3) = -37.5$ kJ/mol [19] and *Benson* group increments.

g) From $BDE(RSCH_2{-}H) = 389$ kJ/mol [29] and ΔBDE as in d).

h) From [30].

i) From $h_f(CH_3SO_2Ph) = -253.4$ kJ/mol [19] and *Benson* group increments.

k) From $BDE(PhSO_2CH_2{-}H) = 411$ kJ/mol g) and increments d).

l) Kindly provided by Dr. *M. Allan*, Fribourg.

m) As $BDE(RCHCl{-}H)$ and $BDE(RCCl_2{-}H)$ from [2c].

n) From $h_f(CH_2{=}CCl_2)$ and $\Delta h_f(CHCl{=}CHCl/CH_2{=}CHCl)$ [19].

o) From $h_f(CH_3CHClCCl_2H)$ and $\Delta h_f(CH_3CHCl_2/CH_3CH_2Cl)$ [19].

p) From [31].

q) From $h_f(CH_2{=}CCl_2)$ and $\Delta h_f(CH_3CH{=}CH_2/CH_2{=}CH_2)$ [19].

r) From $h_f(CH_3CHCl_2)$ and $\Delta h_f((CH_3)_2CHCH_3/CH_3CH_3)$ [19].

s) From $h_f(CH_3CH_2CH_2CN)$ and $\Delta h_f(CH_3CH_2CH_2CH_3/(CH_3)_2CHCH_2CH_3)$ [19].

t) As $BDE(RCHCN{-}H)$ from [2c].

we have no means to specify possible solvent effects. Now, for $\cdot CH_2CN$ *Radom* and coworkers state that the barrier heights are strongly influenced both by electrophilic polar and by enthalpy effects of the alkene substituents, because the barriers are lower than those calculated for the addition of the methyl radical for the same enthalpy, and because plots of E_a *vs.* H_r and *IP* gave complete scatter. We agree with their principle conclusion that enthalpy and polar effects operate, but do find a good correlation with H_r which is of predictive power and only minor specific substituent effects pointing to the radical's electrophilicity. For three alkenes, which can be compared directly, the calculated reaction enthalpies agree with our estimates with insignificant deviations of up to 5 kJ/mol. This is reassuring, but, for acrylonitrile, the calculated barrier is significantly lower by 16 kJ/mol. The ordering of the activation energies agrees with our work, but it is very disturbing that the calculated barriers for the addition of $\cdot CH_2CN$ to all four comparable alkenes are significantly higher than the experimental data by 11 to 15 kJ/mol. This difference means that the gas-phase rate constants should be two to three orders of magnitude lower than we observe, if our frequency factor is accepted or would require frequency factors of 10^{11}–10^{12} $M^{-1}s^{-1}$ which are way out of usual ranges. Otherwise, very large solvent effects must operate which are different for the educts and the transition states. This is hard to accept, since we found only minor influences of the solvent for the addition of the strongly nucleophilic *tert*-butyl radical to acrylonitrile [2a]. Hence, we must conclude that calculated barriers and their specific dependence on the substituents do not yet reflect the details of the reactivity of $\cdot CH_2CN$ in solution. For $\cdot CH_2OH$ and *tert*-butyl, the calculated enthalpies and barriers are closer to our values [2c]. However, whereas we obtain good correlations with the alkene *EA* and no significant correlation with the reaction enthalpy which can be rationalized *via* the correlation diagram, *Radom* and coworkers [10] find in contrast that the selectivity also of these very nucleophilic species should be controlled by the enthalpy and note only a general decrease of the barrier by polar effects.

We acknowledge the financial support by the *Swiss National Foundation for Scientific Research*, thank Mrs. *I. Verhoolen* for product analyses, and appreciate helpful discussions with *L. Radom*, Australian National University.

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