142. The Addition of *tert*-Butyl ($Me_3\dot{C}$) and (*tert*-Butoxy)carbonylmethyl ($Me_3CO_2C\dot{C}H_2$) Radicals to Alkynes in Solution Studied by ESR Spectroscopy

by **Herbert Rubin** and **Hanns Fischer***

Physikalisch-chemisches Institut der Universität Zürich, Winterthurerstrasse 190, CH-8057 Zürich

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Absolute rate constants and their temperature dependence are determined by time-resolved electron spin resonance for the addition of $Me_3\dot{C}$ to 20 and of $Me_3CO_2C\dot{C}H_2$ to six mono- and disubstituted alkynes in solution. For $Me_3\dot{C}$ the rate constants show polar alkyne-substituent effects which are, however, weaker than for the corresponding alkenes. For $Me_3CO_2\dot{C}H_2$, the rate constants do not vary strongly with alkyne substitution and probably increase with increasing reaction exothermicity. Both radicals react generally slower with alkynes than with alkenes which is discussed in terms of the state correlations. Several vinyl-type radical adducts of $Me_3\dot{C}$ to alkenes are characterized by electron spin resonance, and their spectral data indicate linear or bent configurations of the radical carbon depending on the substitution.

1. Introduction. – In recent years, inter- and intramolecular additions of C-centered radicals to multiple C,C bonds have found many useful synthetic applications [1]. The planning of a successful synthesis requires the consideration of the addition rate constants, and for additions to alkenes including intramolecular cyclizations large series of data are available [2]. On the other hand, only a few rate constants are known for the corresponding additions to alkynes which are also of use, especially in sequential radical cyclizations [1]. Therefore, it is also unknown whether they are influenced similarly by the enthalpic, steric and polar substituent effects which are established for the additions to alkenes [3].

We have now extended our work on the addition of C-centered radicals by time-resolved electron spin resonance (ESR) and other methods [4] to a study of alkynes. Two radicals have been chosen: firstly, the *tert*-butyl radical $Me_3\dot{C}$ which is highly nucleophilic so that the addition rate constants to alkenes increase dramatically with increasing alkene electron affinity [4a], and, secondly, the (*tert*-butoxy)carbonylmethyl radical ($Me_3CO_2C\dot{C}H_2$) which show little polar effects in alkene additions. Instead, its rate constants increase with increasing reaction exothermicity [4e].

To establish the nature of the reaction and to determine the reaction site, we have also attempted to detect the adducts of the radicals to the alkynes by ESR. These vinyl-type radicals are highly reactive and usually difficult to observe, but, for the addition of $Me_3\dot{C}$, 15 new vinyl radicals were found. Their ESR parameters are discussed in terms of the configuration of the radical centre which may be bent or linear. Furthermore, we also report several newly determined rate constants for the addition of the $Me_3\dot{C}$ to alkenes.

2. Experimental. – All arrangements and procedures for steady-state and time-resolved ESR were as described in [4]. The radicals $Me_3\dot{C}$ and $Me_3CO_2C\dot{C}H_2$ were generated by photolysis of the corresponding disubstituted ketones. These undergo type-I cleavage from a short-lived triplet state followed by a fast decarbonylation of the alkyl-radical fragment [4a, e].

$$R_2CO \xrightarrow{h\nu} R{-}\dot{C}O + \dot{R} \longrightarrow CO + 2\,\dot{R} \qquad (1)$$

Most of the chemicals were commercially available and used in the purest available forms. 3-Phenylprop-2-ynenitrile and ethyl prop-2-ynoate were synthesized following literature prescriptions [5]. All solns. were freed from O_2 by purging with He prior to use. The *g* factors of the product radicals were determined relative to $g = 2.0027$ for $Me_3\dot{C}$ which was simultaneously present in the spectra.

In steady-state experiments aiming at the observation of the radical adducts to alkynes, ketone concentrations of 0.3–0.6M and rather high substrate concentrations ≥ 0.1M were employed. For the kinetic runs, a lower ketone concentration of usually *ca.* 0.1M and lower alkyne concentrations were used. As in [4], the addition rate constants were obtained by fitting the decay of the reacting radical $\dot{R}$ to the appropriate mixed second- and pseudo-first-order rate law, and, for most substrates, it was ensured by variation of the substrate concentration [S] that the extracted pseudo-first-order lifetime τ_l obeyed the linear relation $\tau_l^{-1} = \tau_{l0}^{-1} + k$ [S]. Here, τ_{l0} comprises side reactions with the solvent and the parent ketone. An example is given in *Fig. 1*. Several alkynes reacted so fast that [S] could be varied only in a narrow range. In these cases, substrate depletion may have occurred, and, hence, the very high rate constants may be subject to larger errors and represent lower limits, only.

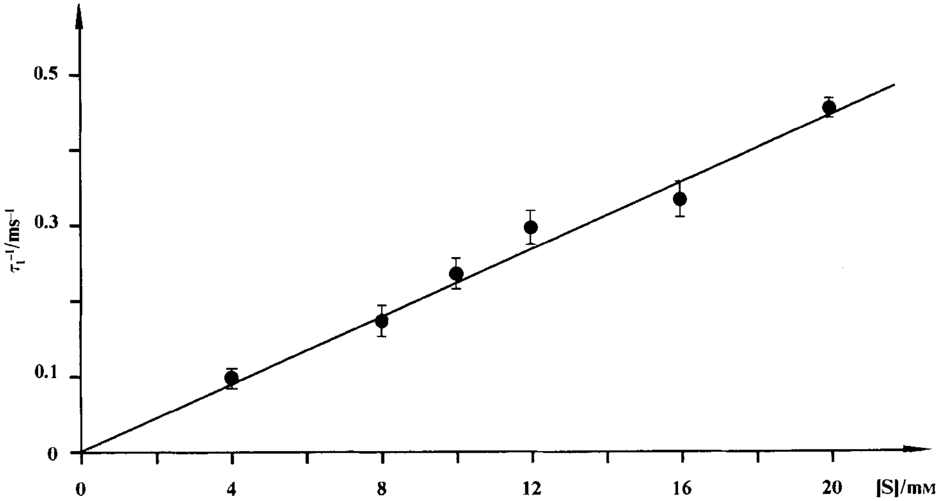


Fig. 1. *Pseudo-first-order plot for the addition of $Me_3\dot{C}$ to PhC≡CH in 1,2-epoxypropane at 297 K*

Auxiliary semiempirical quantum-chemical calculations were performed with the AM1 routine.

3. ESR Spectra of Vinyl-Type Radicals.

– The vinyl-type species $RXC{=}\dot{C}Y$ formed by addition of radicals $\dot{R}$ to alkynes XC≡CY are known to readily abstract H-atoms, to add to the parent alkyne and to undergo internal rearrangements to alkyl radicals [6]. Therefore, for the solvents ethanol and i-PrOH, the ketone photolysis in the presence of alkynes yielded only $Me\dot{C}HOH$ and $Me_2\dot{C}OH$ radicals. Also, for $Me_3CO_2C\dot{C}H_2$, relatively complicated spectra were obtained in all solvents which could not be ascribed to vinyl species and are probably due to their reaction products with the parent ketone.

Clear signatures of vinyl-type radicals resulted only during the addition of $Me_3\dot{C}$ to 13 alkynes and, in part, only at low temperatures. Spectra are given in *Figs. 2–4* and the radical properties are collected in *Table 1*. For comparison, we have also generated two adducts of the $Me_2\dot{C}H$ radical using the photolysis of 2,4-dimethylpentan-3-one as radical source.

The five vinyl-type radicals found during the reaction with monosubstituted alkynes HC≡CY exhibit one large proton coupling constant which is typical for the *β*-proton of

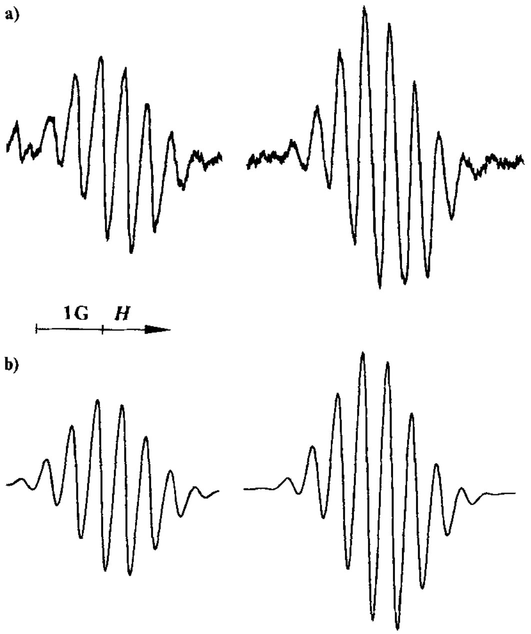


Fig. 2. *ESR Spectra* a) *observed during photolysis of 0.3* M (t-Bu)$_2$CO *in 3,3-dimethylbut-1-yne at 303 K* (the two line groups are separated by the large β-proton coupling constant of 54 G), b) *simulation*

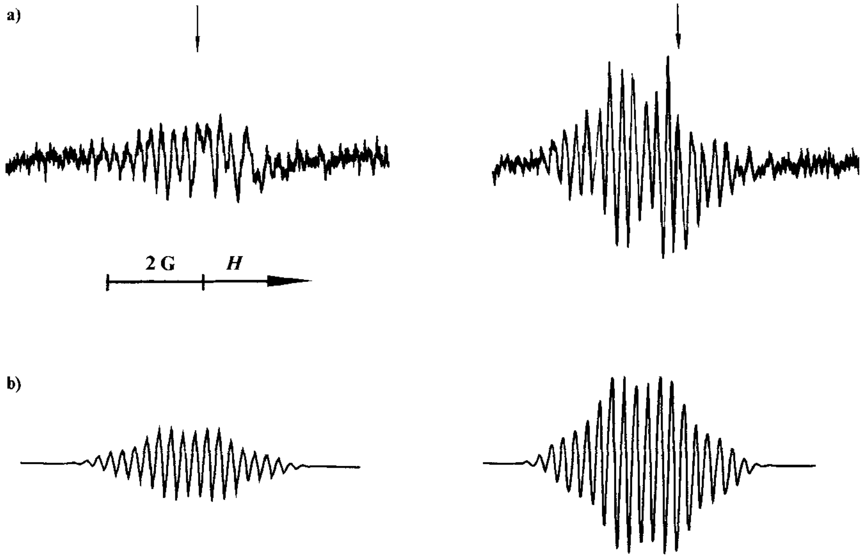


Fig. 3. *ESR Spectra* a) *observed during photolysis of 0.6* M (t-Bu)$_2$CO *and 0.4* M *$HC \equiv CCO_2Me$ in 1,2-epoxypropane at 173 K* (arrows denote line positions of $Me_3\dot{C}$, and the two line groups are separated by the large β-proton coupling constant of 51 G), b) *simulation*

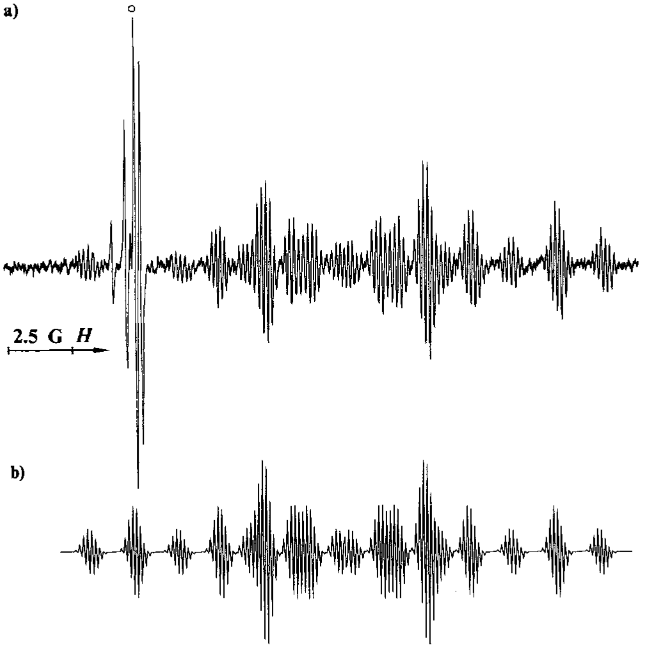
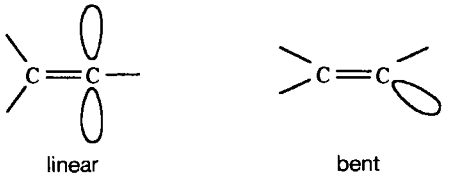


Fig. 4. *Highfield half of ESR Spectra* a) *observed during photolysis of 0.4*M (t-Bu)$_2$CO *and 0.8*M *PhC≡CH in heptane at 286 K* (o: lines of $Me_3\dot{C}$), b) *simulation*

$RCH{=}\dot{C}Y$[1]). Hence, the addition occurs selectively at the unsubstituted C-atom as it is known from product studies[2]). The radicals derived from $HC{\equiv}CPh$ and $R'O_2CC{\equiv}CPh$ show similar couplings to the ring protons, *i.e.*, for the latter alkyne the addition occurs to the carboxy-substituted site. In keeping with the facile addition to alkynedioates [6], these compounds lead to strong vinyl-type spectra which were observable only at low temperatures, however. At room temperature, secondary processes interfered. With $MeC{\equiv}CCO_2Me$, we observe a vinyl-type species with a coupling of 21.97 G to a Me group. This is similar to the known Me couplings of $CH_2{=}\dot{C}Me$ [9] and $HO(Me)C{=}\dot{C}Me$ [10]. Hence, $Me_3\dot{C}$ adds to the site of CO_2R substitution which parallels the selectivity of additions to $Me_3CC{\equiv}CCO_2R'$ [11].

Depending on the substitution vinyl-type radicals adopt linear or bent structures, *i.e.*, are π-or σ-radicals [8–11]. In the latter case, they may rapidly invert at the radical centre. Usually, the bent structure is preferred for Y = H, alkyl, Hal and OMe, whereas vinyl radicals with Y = Ph, CO_2R and CN are considered linear, though the latter conclusion has been questioned [11] [12].



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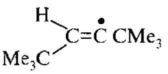
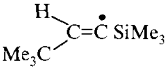
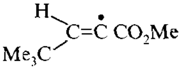
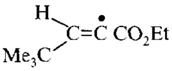
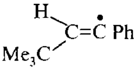
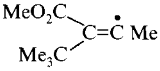
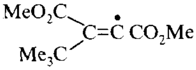
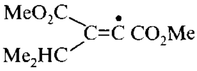
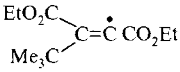
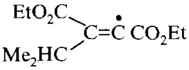
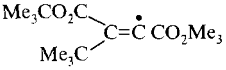
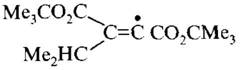
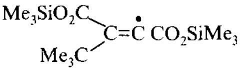
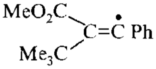
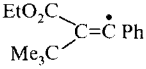
[1]) For hyperfine coupling constants and g factors of vinyl-type radicals, see [7].

[2]) For representative studies, see [8].

Table 1. *g Factors* (± 0.0001) *and Coupling Constants* a (± 0.05 G) *of Vinyl-Type Radicals Formed by Addition of* $Me_3\dot{C}$ *and* $Me_2\dot{C}H$ *Radicals to Alkynes*

Radical	T [K]	g	Coupling constants [G]	
	303a)	2.0023	$1H_\beta$: 9H (*t*-Bu):	54.0 0.38
	298b)	2.0024	$1H_\beta$: 9H ($SiMe_3$): 9H (*t*-Bu):	56.5 0.46 0.18
	173c)	2.0031	$1H_\beta$: 3H (Me): 9H (*t*-Bu):	51.0 1.0 0.25
	173c)	2.0031	$1H_\beta$: 2H (Et): 9H (*t*-Bu):	51.0 1.0 0.25
	286b)	2.0024	$1H_\beta$: $2H_o$: $2H_m$: $1H_p$: 9H (*t*-Bu):	37.8 5.19 1.79 6.33 0.175
	298b)	2.0021	3H (Me): 9H (*t*-Bu):	21.97 0.53
	172c)	2.0031	3H (Me): 9H (*t*-Bu):	1.32 0.625
	169c)	2.0032	3H (Me): $1H_\gamma$: 6H (2 Me):	1.23 0.55 0.35
	169c)	2.0031	2H (Et): 9H (*t*-Bu):	1.30 0.65
	169c)	2.0033	2H (Et): $1H_\gamma$: 6H (2 Me):	1.28 0.60 0.35
	169c)	2.0031	9H (*t*-Bu):	0.60
	171c)	2.0033	$1H_\gamma$: 6 H (2 Me):	0.38 0.43
	177c)	2.0032	9H (*t*-Bu):	0.65
	298b)	2.0025	$2H_o$: $2H_m$: $1H_p$: 9H (*t*-Bu):	5.26 1.82 6.67 0.42
	298b)	2.0025	$2H_o$: $2H_m$: $1H_p$: 9H (*t*-Bu):	5.17 1.80 6.57 0.42

a) In 3,3-dimethylbut-1-yne.

b) In hexane.

c) In 1,2-epoxypropane.

Our data of *Table 1* allow the following structural assignments: $(Me)_3C$-$(MeO_2C)C{=}\dot{C}Me$ must be bent, since it has the particularly low *g* factor of bent vinyl species and the expected [9] [10] Me coupling constant. On the other hand, the radicals $RXC{\equiv}\dot{C}Ph$ must be linear because the couplings to the ring protons are almost identical with those of the benzyl radical $Ph\dot{C}H_2$ [13]. For the radicals of type $RCH{=}\dot{C}Y$, we further note that the β-proton coupling constants vary with the substituents Y as the Me coupling constants of the corresponding alkyl radicals $Me\dot{C}HY$. Combining the data for a(CH) from *Table 1* with a(Me) for $Me\dot{C}HY$ from [7], one obtains the ratios $a(CH)/a(Me) = 2.11$, 2.17, 2.05 and 2.24 for Y = Ph, CMe_3, CO_3R and $SiMe_3$, respectively. A ratio of 2 is expected from the *Heller-McConnell* relation between a_β and the dihedral angle for a π-type radical with the C–H bond eclipsing the $2p_z$ orbital. Hence, $RCH{=}\dot{C}Y$ radicals with Y = CMe_3, CO_2R and $SiMe_3$, also adopt an at least close to linear configuration or rapidly invert at the radical centre. The auxiliary AM1 calculations performed during this work and by others [14] support this view.

Besides the compounds listed in *Table 1*, several other alkynes were employed in the search for vinyl-type radicals. For $PhC{\equiv}CCN$, we obtained a weak spectrum with benzylic-type couplings which is probably due to $Me_3C(NC)C{=}\dot{C}Ph$. For three alkynes with easily abstractable H-atoms, $R'CH_2C{\equiv}CH$, allenyl-type radicals were found. Their properties are given in *Table 2* and are usual for such species. Consequently, in the kinetic experiments only such alkynes were employed for which addition was established by the detection of the adduct radicals or may reasonably by expected as major reaction path, and alkynes with easily abstractable H-atoms were excluded.

Table 2. *g-Factors* (±0.0001) *and Coupling Constants* a (±0.05 G) *of Allenyl Radicals Formed* via *H-Abstraction by* $Me_3\dot{C}$ *Radicals from 1-Alkynes* $HC{\equiv}CCH_2R$

Radical	T [K]	g	a [G]	
$C_3H_7CH{=}C{=}\dot{C}H$	316[a])	2.0028	$1H_\alpha$:	11.5
			$1H_\gamma$:	18.4
			$2H_\delta$:	18.4
			$2H_\varepsilon$:	0.46
$HOCH{=}C{=}\dot{C}H$	295[b])	2.0030	$1H_\alpha$:	9.57
			$1H_\gamma$:	17.4
			1H(OH):	1.14
$Me_3SiOCH{=}C{=}\dot{C}H$	293[c])	2.0031	$1H_\alpha$:	10.13
			$1H_\gamma$:	18.15

[a]) In hex-1-yne. [b]) In i-PrOH. [c]) In hexane.

4. Rate Constants for the Addition of $Me_3\dot{C}$ to Alkynes.

– *Table 3* shows absolute rate constants and activation parameters for the reaction of $Me_3\dot{C}$ with 20 alkynes which we presume to occur by addition to the X-substituted C-atom. Representative plots of rate constants *vs.* temperatures are given in *Fig. 5* together with best fits to the *Arrhenius* law. Several of these plots showed considerable scatter as *Fig. 5, a*, and this was found typically for the very reactive alkynes. For these, the activation parameters are displayed in italics in *Table 3*. With alkyne substitution the rate constants vary by several orders of magnitude. For the monosubstituted alkynes, the average frequency factor $\log (A/\mathrm{M}^{-1}\mathrm{s}^{-1}) = 7.9 \pm 1.5$, if all values, and $\log (A/\mathrm{M}^{-1}\mathrm{s}^{-1}) = 9.1 \pm 0.3$, if only the more reliable ones are used.

Table 3. *Absolute Rate Constants*[a] (at 300 ± 2 K), *Frequency Factors* A[a]) *and Activation Energies* E_a[a]) (Temperature Range 260–330 K) *for the Addition of* $Me_3\dot{C}$ *to Alkynes* (X–C≡C–Y) *in i-PrOH*

X	Y	*c* [mM]	k_{300} [$M^{-1}s^{-1}$]	log (A/$M^{-1}s^{-1}$)	E_a [kJ/mol]
H	CMe_3	500–2000	220 (10)	*6.1 (0.8)*[c]	*22.3 (1.9)*[c]
H	CPhOHMe	100–1000	380 (50)	9.4 (0.6)	38.4 (1.4)
H	$SiMe_3$	20–80	2400 (400)	8.9 (0.8)	30.8 (2.0)
H	CH_2Cl	25–200	4000 (400)	9.5 (0.4)	33.7 (0.9)
H	Ph	4–20	21000 (10^3)[b]	8.7 (0.3)	23.8 (0.6)
H	CO_2Me	0.4–1.4	180000 ($3\cdot10^4$)[b]	*6.0 (0.4)*	*6.9 (0.8)*
H	CO_2Et	0.4–2.0	200000 ($2\cdot10^4$)[b]	*6.7 (0.9)*	*10.7 (2.2)*
Me	$SiMe_3$	500–2000	40 (5)	7.1 (1.4)	30.3 (3.8)
Me	Ph	250–1000	430 (50)	7.2 (0.9)	26.4 (2.1)
CO_2Me	Me	100–600	520 (50)[b]	8.3 (0.7)	29.6 (1.5)
$SiMe_3$	Ph	100–1000	600 (60)	6.8 (0.7)	22.6 (1.7)
Ph	Ph	100	1000 (200)	*9.2 (0.4)*	*37.7 (1.1)*
CH_2Cl	CH_2Cl	20–1000	2000 (200)	7.9 (0.9)	25.5 (2.0)
CO_2Me	Ph	1–10	50000 ($3\cdot10^3$)[b]	8.4 (0.3)	18.3 (1.6)
CO_2Et	Ph	1–10	42000 ($5\cdot10^3$)[b]	8.4 (0.7)	18.9 (1.6)
CO_2tBu	CO_2tBu	0.2–3	270000 ($5\cdot10^4$)[b]	*7.0 (0.6)*	*11.6 (1.5)*
CO_2SiMe_3	CO_2SiMe_3	0.5–5	230000 ($3\cdot10^4$)	*9.3 (1.2)*	*22.0 (2.7)*
CO_2Me	CO_2Me	0.1–0.5	570000 (10^5)[b]	*8.1 (1.7)*	*14.7 (4.7)*
CO_2Et	CO_2Et	0.1–1	540000 ($8\cdot10^4$)[b]	*6.7 (1.0)*	*8.1 (2.5)*
CN	Ph	0.1–2	200000 ($3\cdot10^4$)	*6.9 (0.7)*	*9.2 (1.7)*

[a] Standard deviations in units of the last digital number given in brackets. [b] k_{300} in 1,2-epoxypropane. [c] *Arrhenius* parameters in italics were determined from temperature dependencies with substantial scatter of the data and may be subject to error compensation.

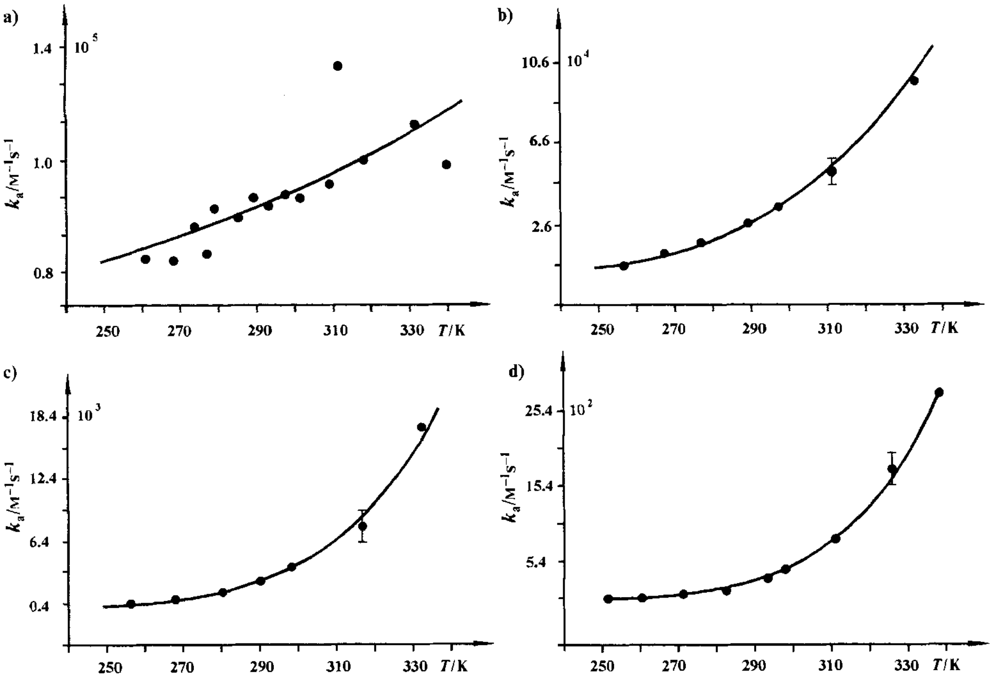


Fig. 5. *Temperature dependence of four addition rate constants of* $Me_3\dot{C}$ *to alkynes in i-PrOH*; a) $HC{\equiv}CCO_2Et$, b) $HC{\equiv}CPh$, c) $HC{\equiv}CCH_2Cl$, d) $HC{\equiv}CCMe_3$

As far as we know, there are no other data for $Me_3\dot{C}$ additions to alkynes in solution. Evaluated rate data for the gas phase are $k_{300} = 40\ \text{M}^{-1}\text{s}^{-1}$ and $\log A = 7.9$ for the addition to $H_2C{=}CH_2$ [15] in reasonable agreement with the trends seen in *Table 3*. The related $Me_2\dot{C}H$ radical adds to butynedioic acid in H_2O with $k_{300} \approx 10 \cdot 10^6\ \text{M}^{-1}\text{s}^{-1}$ [6], and this order of magnitude also agrees with our findings.

5. Rate Constants for the Addition of $Me_3CO_2C\dot{C}H_2$ to Alkynes. – *Table 4* displays the absolute rate constants and their *Arrhenius* parameters. As stated for $Me_3\dot{C}$, some of the data showed substantial scatter. For the four monosubstituted alkynes the rate constants vary comparatively little with the substituents, but the ordering is the same as for $Me_3\dot{C}$ (*Table 3*). The average frequency factor for alkynes $HC{\equiv}CY$ obeys now $\log (A/\text{M}^{-1}\text{s}^{-1}) = 9.2 \pm 0.4$.

Table 4. *Absolute Rate Constants*[a] (at 300 ± 2 K), *Frequency Factors* A[a] *and Activation Energies* E_a (Temperature Range 280–340 K) *for the Addition of* $Me_3CCO_2C\dot{C}H_2$ *to Alkynes* ($X{-}C{\equiv}C{-}Y$) *in MeCN*

X	Y	c [mM]	k_{300} [$\text{M}^{-1}\text{s}^{-1}$]	$\log (A/\text{M}^{-1}\text{s}^{-1})$	E_a [kJ/mol]
H	CMe_3	2.5–10	12000 (4500)	9.5 (10)	31.7 (3.3)
H	$SiMe_3$	1–10	22000 (4000)	9.4 (0.3)	29.7 (2.0)
H	CH_2Cl	1–5	24000 (2500)	*9.2 (0.6)*[b]	*28.3 (3.7)*[b]
H	CO_2Et	1–5	51000 (2000)	8.5 (0.4)	21.6 (1.0)
CO_2Me	Me	5–20	5000 (500)	*8.0 (3.0)*	*25.1 (7.5)*
Ph	Ph	5	11000 (1000)	*6.1 (0.8)*	*11.8 (5.4)*

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

[b] *Arrhenius* parameters in italics were determined from temperature dependencies with substantial scatter of the data and may be subject to error compensation.

6. Discussion of the Addition-Rate Data. – Several *ab initio* molecular-orbital calculations for the transition state of the addition of H•, HO• and $H_3\dot{C}$ radicals to $HC{\equiv}CH$ are available [16]. As for alkenes, the transition state lies early on the reaction coordinate and shows a long bond of *ca.* 230 pm between the radical and the attacked C-atom, whereas the angle of attack is already close (116°) to the R–C–C angle of the product radical. The $C{\equiv}C$ bond is still short, and there are bending deformations at both C-atom. The similarity of alkyne and alkene transition states suggests that addition rates of the radicals to alkenes and alkynes are governed by the same effects.

To extract these from the data, we first consider the frequency factors. For addition to alkenes of type $CH_2{=}CXY$, they do not vary significantly with alkene substitution, and averages of $\log (A/\text{M}^{-1}\text{s}^{-1}) = 7.3 \pm 0.4$ and $\log (A/\text{M}^{-1}\text{s}^{-1}) = 8.1 \pm 0.1$ were established for the addition of $Me_3\dot{C}$ and $Me_3CO_2C\dot{C}H_2$, respectively [4a,e]. The data of *Tables 3* and *4* for the corresponding alkynes $HC{\equiv}CY$ show a larger spread, but this is probably due to compensation errors of the *Arrhenius* parameter. The averages given above indicate that the frequency factors for additions to alkynes are about one order of magnitude larger than those for alkenes. The calculations of *Arnaud et al.* [16] for the additions of $H_3\dot{C}$ to $H_2C{=}CH_2$ and $HC{\equiv}CH$ predict the same trend. Grossly, it is due to a lower loss of rotational entropy of $HC{\equiv}CH$ on approach to the transition state, which is a natural consequence of its linear structure. Hence, the frequency factors are reasonable, and the variations of the rate constants with different substituents are mainly caused by changing activation energies both for alkenes and alkynes. For higher substituted compounds, the frequency factors may vary more than in the ranges given above.

In *Table 5*, we now compare the rate constants for alkene and alkyne additions. Part of the alkene data were determined newly in this work. In agreement with the common notation [1] [3] [8], but with some exceptions, alkynes are less reactive than alkenes. In view of the higher frequency factors, this means that their activation barriers are substantially higher, and this has also been found in the *ab initio* calculations [16].

Table 5. *Rate Constants* (at 300 K) *for the Addition of* $Me_3\dot{C}$ *and* $Me_3CO_2\dot{C}CH_2$ *to Alkynes* ($XC{\equiv}CY$) *and Alkenes* ($XHC{=}CHY$)

Radical	X	Y	k_{yne}	k_{ene}	k_{yne}/k_{ene}
$Me_3\dot{C}$	H	H	40.3	30.1	1.34a)
$Me_3\dot{C}$	H	CMe_3	220	160b)	1.20
$Me_3CO_2C\dot{C}H_2$	H	CMe_3	$1.2 \cdot 10^4$	$3.5 \cdot 10^4$c)	0.34
$Me_3\dot{C}$	H	$SiMe_3$	$2.4 \cdot 10^3$	$9.6 \cdot 10^3$b)	0.25
$Me_3CO_2C\dot{C}H_2$	H	$SiMe_3$	$2.2 \cdot 10^4$	$8.9 \cdot 10^4$c)	0.25
$Me_3\dot{C}$	H	CH_2Cl	$4 \cdot 10^3$	$8.2 \cdot 10^3$	0.49
$Me_3\dot{C}$	H	Ph	$2.1 \cdot 10^4$	$1.3 \cdot 10^5$b)	0.16
$Me_3\dot{C}$	H	CO_2Me	$1.8 \cdot 10^5$	$1.0 \cdot 10^6$	0.16
$Me_3CO_2C\dot{C}H_2$	H	CO_2Et	$5.1 \cdot 10^4$	$4.9 \cdot 10^5$)c)	0.41
$Me_3\dot{C}$	Me	CO_2Me	$5.2 \cdot 10^2$	$6.9 \cdot 10^3$d)	0.08
$Me_3\dot{C}$	Me	Ph	$4.3 \cdot 10^2$	$1.8 \cdot 10^3$e)	0.24
$Me_3\dot{C}$	CO_2Me	Ph	$5 \cdot 10^4$	$1.5 \cdot 10^5$e)	0.34
$Me_3\dot{C}$	CN	Ph	$2 \cdot 10^5$	$3.6 \cdot 10^5$e)	0.56
$Me_3\dot{C}$	CO_2Me	CO_2Me	$5.7 \cdot 10^5$	$5.3 \cdot 10^5$e)	1.10f)

a) Gas phase [15]. b) [4a]. c) [4b]. d) (*Z*)/(*E*)-Mixture. e) (*E*)-Isomer. f) A ratio of 0.19 for unspecified alkene isomer has also been reported [8c].

Now, for alkenes of the type $CH_2{=}CXY$, the activation barriers vary because of enthalpic and polar substituent effects [1] [2] [4] [17]. If the first effect dominates, the activation energy decreases with increasing exothermicity of the addition, and there are no special deviations from this behaviour for strongly electron-donating or -withdrawing substituents. In [4e], $Me_3CO_2C\dot{C}H_2$ was found to react accordingly. On the other hand, for $Me_3\dot{C}$ and other nucleophilic radicals [4a, b], as well as for electrophilic species [18], the correlation with the reaction enthalpy is weak, and the polar effect dominates the trends, though this has partly been questioned on the basis of calculated barriers [17]. This polar effect is due to partial electron transfer in the transition state and can be represented by a mixture of the configurations $R^+A^{-\cdot}$ and $R^-A^{+\cdot}$. For strongly nucleophilic radicals, the barriers decrease with increasing electron affinity of the alkene, and the styrenes, for which the exothermicity should be larger, react slower than acrylates and acrylonitriles. In terms of a frontier MO description, the polar effects amount to stabilizing SOMO-LUMO and SOMO-HOMO interactions. Additions to higher substituted alkenes are also influenced by steric hindrance [3] [4].

To estimate the reaction enthalpies H_r needed for an analysis, we consider the overall reaction

$$R{-}H + A \longrightarrow \dot{R} + \dot{H} + A \xrightarrow{H_r} R\dot{A} + \dot{H} \longrightarrow RA{-}H \tag{2}$$

as before [4]. H_r can be expressed by enthalpies of formation H_f of the radical precursor R–H, the alkene or alkyne A and the product RA–H, and bond dissociation energies (*BDE*) of R–H and RA–H as

$$H_r = H_f(\mathrm{RA{-}H}) - H_f(\mathrm{RH}) - H_f(\mathrm{A}) + BDE(\mathrm{RA{-}H}) - BDE(\mathrm{R{-}H}) \qquad (3)$$

In earlier publications, we have listed these energy values for several radical additions to various alkenes [4] and obtained, *e.g.*, $H_r = -98$ kJ/mol, -79 kJ/mol and -72 kJ/mol for the addition of $H_3\dot{C}$, $Me_3\dot{C}$ and $Me_3CO_2C\dot{C}H_2$, respectively, to ethene. For alkynes, the corresponding estimations are hindered by the fact that the *BDE* of C–H bonds of substituted alkenes RXC=CY–H are unknown. As far as we know, *BDE* = 459 kJ/mol [19] for $H_2C{=}CH{-}H$ is the only available value. Using this for RHC=CH–H also and the other enthalpies given before [4e] or taken from [20], the exothermicity of the addition to HC≡CH is estimated as $H_r = -110$ kJ/mol, -91 kJ/mol and -84 kJ/mol, respectively, for the radicals given above. Obviously, the additions to HC≡CH are more exothermic than those to $H_2C{=}CH_2$, as has also been calculated [16]. This is in contrast to the larger reaction barriers. Presumably, it holds generally for alkynes HC≡CY *vs.* alkenes $H_2C{=}CHY$, and in this respect their behaviour is contrathermodynamic [16].

Missing *BDE* of RXC=CY–H were then calculated using AM1. Since this method underestimates the *BDE* of $H_2C{=}CH_2$ by 57 kJ/mol, all calculated values were augmented accordingly. For most substituents Y, the *BDE* of RXC=Y–H were found lower than that of $H_2C{=}CH_2$, and they varied similarly with the substituents as for alkanes RXHX–CYH–H. The largest decrease was obtained for Y = Ph, as expected from the benzylic structure of the Ph- substituted vinyl radicals ascertained above. However, for Y = CO_2R no decrease of the *BDE* was found for the alkenes, whereas it amounts to *ca.* 38 kJ/mol for alkanes [4]. This casts doubt on the validity of the AM1 results, and correspondingly, H_r values derived from them were taken as roughly indicative, only. The comparison with the rate data for additions to alkynes HC≡CY given in *Tables 3* and *4* then showed that for $Me_3CO_2C\dot{C}H_2$ the barriers may correlate with the reaction enthalpy as it was found for the addition of this radical to alkenes [4e]. However, the few data and their small spread do not allow a firm conclusion. For $Me_3\dot{C}$, the reaction enthalpy is not the dominant factor since PhC≡CH reacts considerably slower than acetylenes substituted by CO_2R groups.

In search for polar effects, we now attempt to correlate the addition rate constants with the alkyne electron affinities (*EA*) and ionization potentials (*IP*). They are given in *Table 6*, together with those of the corresponding alkenes. For the alkynes, the *EA* values are lower and the *IP* values are higher than for the alkenes and, therefore, lower polar effects are expected [1] [3]. The rate constants of $Me_3CO_2C\dot{C}H_2$ increase with increasing *EA* of alkyne. However, the dependence is very weak and may be fortuitous: firstly, towards alkenes, this radical does not show any nucleophilicity [4e], and, secondly, there is often a strong positive correlation between the reaction enthalpy and the *EA* of the substrate [4] [17]. Hence, the apparent dependence can be due to enthalpy changes which were found of dominating influence for the addition of this radical to alkenes [4e]. *Fig. 6* shows the rate constants for the addition of $Me_3\dot{C}$ radical to monosubstituted alkynes *vs.* their *EA*. The correlation corresponds to

Table 6. *Electron Affinities* (*EA*/eV) *and Ionization Potentials* (*IP*/eV) *of Alkynes* $HC\equiv CX$ *and Alkenes* $H_2C\equiv CHX$ *in the Gas Phase*

X	Alkyne		Alkene	
	EA[a])	*IP*[b])	*EA*[c])	*IP*[b])
H	−2.6	11.4	−1.78	10.5
CMe_3	−2.96	9.8	−1.73	~9.5
$SiMe_3$	−1.84		−1.14	9.5
CH_2Cl	−1.12	10.7		
Ph	−0.34	8.8	−0.25	8.4
CO_2Me	−0.8	10.3	−0.49	9.9

[a]) [21]. [b]) [20]. [c]) From [20] and previous work.

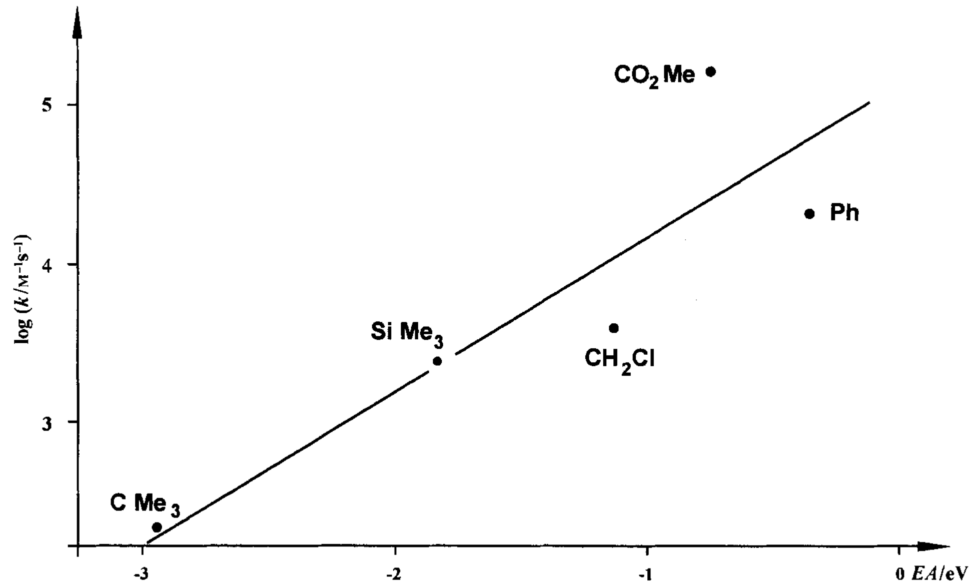


Fig. 6. *Rate constants for the addition of* $Me_3\dot{C}$ *to alkynes* $HC\equiv CX$ *at 300 K* vs. *the electron affinities*

$$\log(k_{300}/\text{M}^{-1}\text{s}^{-1}) = 5.1 + 0.92\ EA/\text{eV} \qquad r = 0.86$$

and is weaker than found for the addition to mono- and 1,1-disubstituted alkenes [4a].

$$\log(k_{300}/\text{M}^{-1}\text{s}^{-1}) = 6.0 + 1.60\ EA/\text{eV} \qquad r = 0.90$$

This is as expected from the larger SOMO-LUMO gap, but ensures the nucleophilic behaviour of $Me_3\dot{C}$ also in its additions to alkynes. Similarly as for other nucleophilic radical additions [4a], the rate constant for $PhC\equiv CH$ is lower than expected from the *EA*, and this is due to the extended charge distribution in $R^+A^{-\cdot}$ which lowers the *Coulomb* attraction in the transition state.

Indirect support for a dominance of the enthalpic factor for $Me_3CO_2C\dot{C}H_2$ and for the nucleophilic polar effect in $Me_3\dot{C}$ additions is also obtained from the different behaviour of these radicals towards mono- and disubstituted alkynes. For the disubstituted alkynes, the rate constants are expected to be lower than for the monosubstituted species because of steric effects, and this is observed for $Me_3CO_2C\dot{C}H_2$ and $Me_3\dot{C}$, if the second substituent is not strongly electron-withdrawing. However, for $Me_3\dot{C}$, the alkynes carrying two electron-withdrawing substituents like CO_2R react as fast as, or even faster than, the monosubstituted counterpart, so that here the polar rate enhancement overrides the steric hindrance.

The foregoing discussion has concentrated on the variations of addition rates with substitution, but the question why alkynes react generally slower than alkenes with the same substituents has not yet been addressed. This can be answered in terms of the state-correlation picture of the transition state [22] which has widely been used in the interpretation of experimental and theoretical reaction barriers [4] [17]. Here, one considers the three-electron system consisting of the unpaired electron of the attacking radical and the two electrons of the attacked bond. The transition state is represented as a mixture of four principal configurations: the reactant ground state ($\dot{R}^1A$), the lowest excited triplet of the attacked bond ($\dot{R}^3A$) and the polar configurations $R^+A^{-\cdot}$ and $R^-A^{+\cdot}$. Along the reaction coordinate, the energy of $\dot{R}^1A$ rises, and this diabatic state correlates with a product state with the new bond locally excited to the triplet state, $\dot{R}^3A$ develops to the product ground state. Taking the unpolar states $\dot{R}^1A$ and $\dot{R}^3A$ alone, the transition state corresponds to an avoided level crossing, and its energy should be influenced by the triplet excitation energy of A, ΔE_{ST}, and the reaction enthalpy H_r. Low values of ΔE_{ST}, and large reaction exothermicities lower the barrier. Contributions of the polar configurations further reduce it and become prominent if these states are of low energies. Now, for alkynes the additions are *ca.* 10–15 kJ/mol more exothermic than the additions to alkenes, and this should lead to a general rate enhancement. However, alkynes also have larger HOMO-LUMO gaps and, therefore, larger singlet to triplet excitation energies. *E.g.*, ΔE_{ST} of PhC≡CPh is by *ca.* 30 kJ/mol larger than ΔE_{ST} of (*Z*)-stilbene [23]. If this difference holds generally for alkyne-alkene pairs, one expects that the effect of the enlarged singlet-triplet gap overrides the effect of the increased reaction enthalpy and causes a larger barrier. Moreover, for alkynes, the energies of the polar states $IP(\dot{R}) - EA(A)$ and $IP(A) - EA(\dot{R})$ are higher than for alkenes (*Table 6*). Hence, they contribute less to the lowering of the barrier, *i.e.*, the unfavourable triplet- and polar-state energies explain the contrathermodynamic behaviour.

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REFERENCES

[1] B. Giese, 'Radicals in Organic Synthesis: Formation of Carbon–Carbon Bonds', Pergamon Press, Oxford, 1986; D.P. Curran, 'Comprehensive Organic Synthesis', Eds. B.M. Trost and I. Fleming, Pergamon Press, Oxford, 1991, Vol. 4, pp. 715–831.

[2] Landolt-Börnstein, 'Radical Reaction Rates in Liquids', Ed. H. Fischer, New Series, Vol. II/13a, II/18a, II/18b, Springer, Berlin, 1984, 1995.

[3] B. Giese, *Angew. Chem. Int. Ed.* **1983**, *22*, 753.

[4] a) K. Münger, H. Fischer, *Int. J. Chem. Kinet.* **1985**, *17*, 809; H. Fischer, 'Substituent Effects in Radical Chemistry', Eds. H.G. Viehe, Z. Janousek and R. Mérényi, Reidel, Dordrecht, 1986; A. Salikhov, H. Fischer, *Appl. Magn. Reson.* **1993**, *5*, 445; b) K. Héberger, H. Fischer, *Int. J. Chem. Kinet.* **1993**, *25*, 93; J.Q. Wu,

H. Fischer, *ibid.* **1995,** *27,* 167; S.N. Batchelor, H. Fischer, *J. Phys. Chem.* **1996,** *100,* 9794; c) K. Héberger, M. Walbiner, H. Fischer, *Angew. Chem. Int. Ed.* **1992,** *31,* 635; M. Walbiner, J. Q. Wu, H. Fischer, *Helv. Chim. Acta* **1995,** *78,* 910; d) T. Zytowski, H. Fischer, *J. Am. Chem. Soc.* **1996,** *118,* 437; e) J.Q. Wu, I. Beranek, H. Fischer, *Helv. Chim. Acta* **1995,** *78,* 194.

[5] A.I. Vogel, *J. Chem. Soc.* **1948,** 607; G. Lohaus, *Chem. Ber.* **1967,** *100,* 2719.

[6] J. Foxall, B.C. Gilbert, H. Kazarians-Moghaddam, R.O.C. Norman, W.T. Dixon, G.H. Williams, *J. Chem. Soc., Perkin Trans. 2* **1980,** 273; B.C. Gilbert, D.J. Parry, *ibid.* **1988,** 875, and ref. cit. therein.

[7] Landolt-Börnstein, 'Magnetic Properties of Free Radicals', Eds. H. Fischer and K.-H. Hellwege, New Series, Vols. II/1, II/9b, II/17b, Springer, Berlin, 1965, 1977, 1986.

[8] a) M. Gazith, M. Szwarc, *J. Am. Chem. Soc.* **1957,** *79,* 3339; b) R.M. Kopchick, J.A. Kampmeier, *ibid.* **1968,** *90,* 6733; c) B. Giese, S. Lachhein, *Angew. Chem.* **1982,** *94,* 780; d) J.O. Metzger, M. Blumenstein, *Chem. Ber.* **1993,** *126,* 2493.

[9] R.W. Fessenden, R.H. Schuler, *J. Chem. Phys.* **1963,** *39,* 2147.

[10] V.N. Belevskii, S.I. Belopushkin, V.I. Feldman, *Dokl. Chem. Proc. Acad. Sci. USSR* (Engl.) **1985,** *281,* 291.

[11] H.G. Korth, J. Lusztyk, K.U. Ingold, *J. Chem. Soc., Perkin Trans. 2* **1990,** 1997.

[12] O. Ito, R. Omori, M. Matsuda, *J. Am. Chem. Soc.* **1982,** *104,* 3934.

[13] H. Paul, H. Fischer, *Helv. Chim. Acta* **1973,** *56,* 1575.

[14] J.O. Metzger, private communication.

[15] D.L. Baulch, C.J. Cobos, R.A. Cox, P. Frank, G. Hayman, T. Just, J.A. Kerr, T. Murrell, M.J. Philling, J. Troe, R.W. Walker, J. Warnatz, *J. Phys. Chem. Ref. Data* **1994,** *23,* 847.

[16] S. Nagase, C.W. Kern, *J. Am. Chem. Soc.* **1979,** *101,* 2544; S. Nagase, C.W. Kern, *ibid.* **1980,** *102,* 4513; R. Arnaud, V. Barone, S. Olivella, A. Solé, *Chem. Phys. Lett.* **1985,** *118,* 573; C. Sosa, H.B. Schlegel, *J. Am. Chem. Soc.* **1987,** *109,* 4193.

[17] M.W. Wong, A. Pross, L. Radom, *J. Am. Chem. Soc.* **1993,** *115,* 11050; M.W. Wong, A. Pross, L. Radom, *Isr. J. Chem.* **1993,** *33,* 415; M.W. Wong, A. Pross, L. Radom, *J. Am. Chem. Soc.* **1994,** *116,* 6284; M.W. Wong, A. Pross, L. Radom, *ibid.* **1994,** *116,* 11983.

[18] K. Riemenschneider, H.M. Bartels, R. Dornow, E. Drechsel-Grau, W. Eichel, H. Luthe, Y.M. Michaelis, P. Boldt, *J. Org. Chem.* **1987,** *52,* 205; D.V. Avila, K.U. Ingold, J. Lustzyk, W.R. Dolbier, H.-Q. Pan, *J. Am. Chem. Soc.* **1993,** *115,* 1577; X.X. Rong, H.-Q. Pan, W.R. Dolbier, B.E. Smart, *ibid.* **1994,** *116,* 4521.

[19] K.M. Ervin, S. Gronert, S.E. Barlow, M.K. Gilles, A.G. Harrison, V.M. Bierbaum, C.H. DePuy, W.C. Lineberger, G.B. Ellison, *J. Am. Chem. Soc.* **1990,** *112,* 5750.

[20] S.G. Lias, J.E. Bartmess, J.F. Liebmann, J.L. Holmes, R.D. Levin, W.G. Mallard, *J. Phys. Chem. Ref. Data* **1988,** *17,* Suppl. 1.

[21] O. Schafer, Ph. D. Thesis, University of Fribourg, 1992.

[22] A. Pross, *Adv. Phys. Org. Chem.* **1985,** *21,* 99; S.S. Shaik, *Progr. Phys. Org. Chem.* **1985,** *15,* 197.

[23] T. Ni, R.A. Caldwell, L.A. Melton, *J. Am. Chem. Soc.* **1989,** *111,* 457.