

## 74. Absolute Rate Constants for the Addition of Benzyl (Ph $\dot{C}H_2$ ) and Cumyl (Ph $\dot{C}Me_2$ ) Radicals to Alkenes in Solution

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Absolute rate constants and their temperature dependence were determined by time-resolved electron spin resonance for the addition of the radicals Ph $\dot{C}H_2$  and Ph $\dot{C}Me_2$  to a variety of alkenes in toluene solution. To vinyl monomers CH<sub>2</sub>=CXY, Ph $\dot{C}H_2$  adds at the unsubstituted C-atom with rate constants ranging from 14 M<sup>-1</sup>s<sup>-1</sup> (ethoxyethene) to 6.7 · 10<sup>3</sup> M<sup>-1</sup>s<sup>-1</sup> (4-vinylpyridine) at 296 K, and the frequency factors are in the narrow range of log (A/M<sup>-1</sup>s<sup>-1</sup>) = 8.6 ± 0.3, whereas the activation energy varies with the substituents from ca. 51 kJ/mol to ca. 26 kJ/mol. The rate constants and the activation energies increase both with increasing exothermicity of the reaction and with increasing electron affinity of the alkenes and are mainly controlled by the reaction enthalpy, but are markedly influenced also by nucleophilic polar effects for electron-deficient substrates. For 1,2-disubstituted and trisubstituted alkenes, the rate constants are affected by additional steric substituent effects. To acrylate and styrenes, Ph $\dot{C}Me_2$  adds with rate constants similar to those of Ph $\dot{C}H_2$ , and the reactivity is controlled by the same factors. A comparison with relative-rate data shows that reaction enthalpy and polar effects also dominate the copolymerization behavior of the styrene propagation radical.

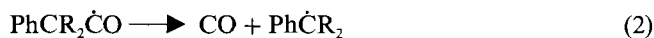
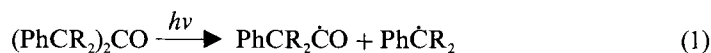
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**1. Introduction.** – The rate constants for the addition of C-centered radicals to C=C bonds, *i.e.*, for one of the most useful radical reactions, are known to be influenced by a complex interplay of polar, enthalpic, and steric effects of radical and alkene substituents [1]. Hence, they are not well understood and far from being reliably predictable. This holds even for the addition to alkenes CH<sub>2</sub>=CXY which occurs regioselectively at the unsubstituted C-atom and does not suffer from steric effects. For this case, *Giese* [1] stressed the importance of polar alkene substituent effects which reflect a stabilization of the transition state by partial electron transfer between radical and alkene. Except for borderline cases [2] or highly stabilized radicals, variations of the reaction enthalpy should exhibit only a minor influence. On the contrary, the results of recent high-level *ab initio* calculations on reaction barriers [3] emphasize the role of the reaction enthalpy as leading factor and reveal only general rate enhancements by polar effects. A more complete understanding requires obviously the availability of large series of rate data and their activation parameters. Therefore, we have measured addition rate constants and their temperature dependence for several prototype alkyl radicals and a large variety of alkenes by time-resolved electron spin resonance in liquid solutions. Hitherto, the easily oxidizable radicals *tert*-butyl (Me<sub>3</sub> $\dot{C}$ ) [4a], hydroxymethyl ( $\dot{C}H_2OH$ ) [4b], and 2-hydroxyprop-2-yl (Me<sub>2</sub> $\dot{C}OH$ ) [4c] were found to exhibit dominating polar effects. They are highly nucleophilic, and their rate constants do not show marked enthalpic effects. In contrast, the additions of the 2-cyanoprop-2-yl radical (Me<sub>2</sub> $\dot{C}CN$ ) follow the reaction enthalpy order [5]. Enthalpic effects also dominate the additions of  $\dot{C}H_2CN$  and (*tert*-butoxy)-carbonylmethyl radicals [6], but there a rate enhancement by electrophilic polar effects is

also observed. Recently, a principal component analysis of most of the data available from our laboratory was performed [7]. In related studies, other groups found prominent electrophilic polar effects for the addition of perfluoroalkyl [8], dicyanomethyl [9], and malonyl [10] radicals.

Here, we present rate data for the addition of the benzyl radical ( $\text{Ph}\dot{\text{C}}\text{H}_2$ ) to a large series of alkenes and of the cumyl radical ( $\text{Ph}\dot{\text{C}}\text{Me}_2$ ) to a few selected compounds. Both radicals are resonance-stabilized and, therefore, the exothermicity of their addition is lower than that for other alkyl radicals. If this were the only controlling factor, very low rate constants would be expected. On the other hand, the radicals have low ionization potentials ( $\text{Ph}\dot{\text{C}}\text{H}_2$ : 7.2 eV,  $\text{Ph}\dot{\text{C}}\text{Me}_2$ : 6.6 eV [11]) as *tert*-butyl and the hydroxyalkyl radicals [4], so that nucleophilic polar effects may enhance the rates. In a preliminary communication of part of this work [12], the rate constants for  $\text{Ph}\dot{\text{C}}\text{H}_2$  at room temperature were, in fact, shown to be low but strongly influenced by a nucleophilic reactivity pattern, and this view was supported by the facile addition of  $\text{Ph}\dot{\text{C}}\text{H}_2$  to  $\text{C}_{60}$  [13]. So far, we did not discuss the role of the reaction enthalpy, however. This is now also considered in detail. Further, we will show that the reactivity of  $\text{Ph}\dot{\text{C}}\text{H}_2$  and  $\text{Ph}\dot{\text{C}}\text{Me}_2$  parallels that of the propagation radical of styrene.

**2. Methods and Results.** – All arrangements and procedures for steady-state and time-resolved ESR were as described in [4–6]. The radicals  $\text{Ph}\dot{\text{C}}\text{H}_2$  and  $\text{Ph}\dot{\text{C}}\text{Me}_2$  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 acyl radical fragment [14].



In accord with the submicrosecond life-time of the acyl radicals,  $\text{Ph}\dot{\text{C}}\text{H}_2$  and  $\text{Ph}\dot{\text{C}}\text{Me}_2$  were the only observable radicals in the absence of alkenes for the whole temperature range covered in this work. They decay by self-termination



at or close to the diffusion controlled limit [15]. Steady-state spectra taken during continuous photolysis with alkene-containing solutions are expected to show the formation of adduct radicals, and these were, in fact, easily detectable for all other alkyl radicals studied before [4–6]. For  $\text{Ph}\dot{\text{C}}\text{H}_2$ , however, we were able to detect and fully characterize the corresponding adduct species only for a few alkenes and only for high concentrations (*ca.* 1M) where polymer precipitation interferes. For the other alkenes, only a decrease of the line intensities of  $\text{Ph}\dot{\text{C}}\text{H}_2$  was noted. This indicates that the addition of  $\text{Ph}\dot{\text{C}}\text{H}_2$  to alkenes is remarkably slow.  $\text{Ph}\dot{\text{C}}\text{Me}_2$  showed the same behavior.

*Table 1* gives the ESR parameters of the benzyl adducts identified in this work. For three alkenes of type  $\text{CH}_2=\text{CXY}$ , we observe addition at the unsubstituted C-atom, only. In keeping with the general experience [1–10], we assume that this also holds for the alkenes for which the adduct radicals were not identified.

Table 1. *g*-Factors ( $\pm 0.0001$ ) and Coupling Constants ( $\pm 0.05$  G) of Adduct Radicals  $\text{PhCH}_2\text{CHZ}\dot{\text{C}}\text{XY}$  from Alkenes ( $\text{HZC}=\text{CXY}$ )

Z	X	Y	T [K]	<i>g</i>	Coupling constants [G]
H	H	CN <sup>a)</sup>	305	2.0031	1 H <sub>z</sub> : 21.1 2 H <sub>β</sub> : 21.75 2 H <sub>γ</sub> : 0.45 <sup>14</sup> N: 3.5
CN	H	CN <sup>a,b)</sup>	306	2.0028	1 H <sub>z</sub> : 20.51 1 H <sub>β</sub> : 19.38 <sup>14</sup> N: 3.5
H	H	CHO <sup>c)</sup>	220	2.0027	1 H <sub>z</sub> : 17.0 1 H <sub>β</sub> : 1.25 2 H <sub>γ</sub> : 21.25
H	Me	CN <sup>a)</sup>	304	2.0030	3 H <sub>β</sub> (Me): 20.5 2 H <sub>γ</sub> : 19.1 <sup>14</sup> N: 3.3

<sup>a)</sup> In *i*-PrOH. <sup>b)</sup> (*E*)-Alkene. <sup>c)</sup> In toluene.

Time-resolved measurements revealed that  $\text{Ph}\dot{\text{C}}\text{H}_2$  and  $\text{Ph}\dot{\text{C}}\text{Me}_2$  decay in the absence of alkenes according to a pure second-order rate law which is ascribed to the self-termination (*Eqn. 3*). Obviously, reactions with the parent ketone or with the solvent toluene do not interfere kinetically. With alkenes present, the second-order decay is perturbed by a pseudo-first-order contribution from the addition reaction. In comparison to our earlier studies [4–6], the kinetic measurements were more tedious because of several reasons: firstly,  $\text{Ph}\dot{\text{C}}\text{H}_2$  and  $\text{Ph}\dot{\text{C}}\text{Me}_2$  show very sharp ESR lines ( $\Delta H_{1/2} \leq 50$  mG), *i.e.*, have rather long relaxation times. Therefore, the line intensities are easily distorted by chemically induced electron spin polarization effects. To minimize these, low ketone concentrations (0.1M) and reduced photolysis intensities were applied which also lowered the signal-to-noise ratios, however. Then, center ESR lines were followed in time which are less affected by polarization. Secondly, the coupling to the ring protons leads to a multitude of splittings which further reduce the individual line intensities. Hence, up to 300 000 concentration *vs.* time profiles had to be accumulated, until kinetic traces with sufficient signal-to-noise ratios were obtained. Finally, the low reactivity of  $\text{Ph}\dot{\text{C}}\text{H}_2$  and  $\text{Ph}\dot{\text{C}}\text{Me}_2$  required the use of rather high alkene concentrations for which unknown side-reactions may interfere. Therefore, special attention was paid to the purity of the alkenes which were purchased (*Fluka*) in the purest available form, freed from stabilizers and distilled before use, where necessary. Dibenzyl ketone (*Fluka*) was recrystallized and dicumyl ketone was synthesized following standard procedures and purified by vacuum distillation and repeated recrystallization.

The rate constants for the addition of  $\text{Ph}\dot{\text{C}}\text{H}_2$  and  $\text{Ph}\dot{\text{C}}\text{Me}_2$  were determined as usual [4–6] from the pseudo-first-order life-times,  $\tau_1$ . For fast reacting alkenes, plots of  $\tau_1^{-1}$  *vs.* alkene concentration were linear, and two examples are given in *Fig. 1*. The rate constants follow from the slopes. However, for a variety of slow reacting alkenes, a measurable pseudo-first-order contribution was obtained only for one fixed and very high alkene concentration. *Arrhenius* parameters were extracted from the temperature dependence of the rate constants (*Fig. 2*).

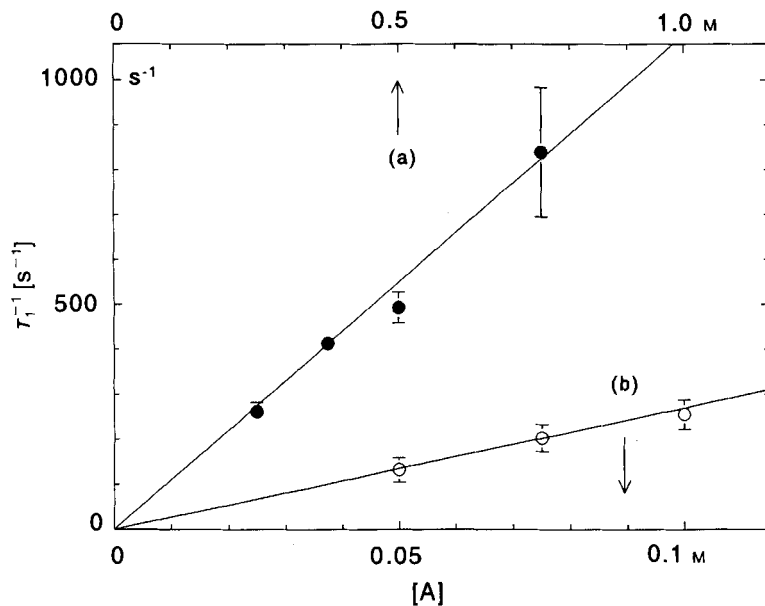


Fig. 1. Pseudo-first-order plots for the addition of  $\text{Ph}\dot{\text{C}}\text{H}_2$  to styrene (●) and of  $\text{Ph}\dot{\text{C}}\text{Me}_2$  to methyl methacrylate (○) at 296 K

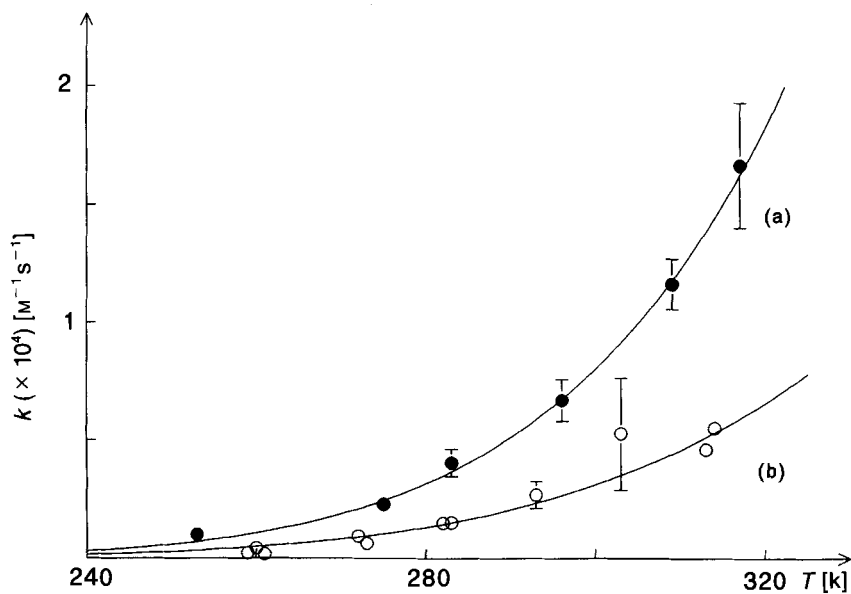


Fig. 2. Temperature dependence of the rate constants for the addition of  $\text{Ph}\dot{\text{C}}\text{H}_2$  to 4-vinylpyridine (●) and of  $\text{Ph}\dot{\text{C}}\text{Me}_2$  to methyl methacrylate (○) and fits to the Arrhenius law

Table 2. Absolute Rate Constants<sup>a)</sup> (at 296±1K), Frequency Factor A<sup>a)</sup>, and Activation Energy E<sub>a</sub><sup>a)</sup> for PhĊH<sub>2</sub> Radical Additions to Alkenes (H<sub>2</sub>C=CXY) in Toluene

X	Y	c [M]	n	k <sub>296</sub> [M <sup>-1</sup> s <sup>-1</sup> ]	log(A/M <sup>-1</sup> s <sup>-1</sup> )	E <sub>a</sub> [kJ/mol]	T [K]
H	OEt	10.44	24	14(2)	10.2(5)	51.5(60)	276–305
H	OCOMe	5–6	40	15(1)	5.9(3)	26.5(30)	270–333
H	<i>t</i> -Bu	7.76	24	18(3)	7.2(3)	33.6(20)	257–311
Me	OMe	10.6	19	21(4)	8.9(4)	42.6(60)	265–303
H	SiMe <sub>3</sub>	3	24	33(8)	8.4(1)	38.8(10)	261–304
H	C <sub>5</sub> H <sub>11</sub>	1–5	15	33(19)	–	–	296
Me	Cl	3	10	43(12)	–	–	296
H	Si(OEt) <sub>3</sub>	0.5–3	28	44(5)	8.4(6)	39.3(80)	261–326
Me	OCOMe	1–3	37	46(6)	7.7(4)	35.4(60)	275–318
H	SO <sub>2</sub> Ph	0.1–0.4	26	290(20)	8.4(2)	31.6(20)	281–325
H	CO <sub>2</sub> Me	0.1–0.6	34	430(80)	7.5(6)	26.6(80)	263–314
Cl	Cl	0.25–0.75	32	460(70)	8.5(6)	33.1(80)	257–311
Me	Ph	0.1–0.75	31	850(110)	9.6(3)	37.8(30)	259–323
H	Ph	0.25–0.75	33	1100(120)	8.6(2)	31.5(10)	263–331
Me	CO <sub>2</sub> Me	0.05–0.15	34	2100(320)	8.1(3)	37.5(30)	259–318
H	CN	0.05–0.2	42	2200(520)	8.9(4)	32.3(50)	263–311
H	Pyridin-2-yl	0.05–0.13	40	2400(240)	11.3(3)	45.5(30)	264–325
H	CHO	0.05–0.15	55	2500(270)	8.5(4)	29.8(40)	261–324
Ph	Ph	0.025–0.1	33	4100(500)	8.8(3)	28.9(20)	261–315
Me	CN	0.025–0.1	40	6600(1100)	8.4(3)	26.6(30)	259–320
H	Pyridin-4-yl	0.025–0.1	29	6700(900)	9.6(2)	32.8(10)	253–318

<sup>a)</sup> Standard deviation in units of the last digit is given in brackets.

Table 2 shows the rate constants for the addition of PhĊH<sub>2</sub> to 21 alkenes CH<sub>2</sub>=CXY and the Arrhenius parameters. We also give the applied alkene concentrations and the number of kinetic experiments evaluated for the individual cases. At 296 K, the rate constants vary from ca. 14 M<sup>-1</sup>s<sup>-1</sup> to ca. 6700 M<sup>-1</sup>s<sup>-1</sup>, and the activation energies from ca. 26 kJ/mol to ca. 51 kJ/mol. The frequency factors range from log(A/M<sup>-1</sup>s<sup>-1</sup>) = 5.9 to log(A/M<sup>-1</sup>s<sup>-1</sup>) = 11.3 but most of the data are within 8 ≤ log(A/M<sup>-1</sup>s<sup>-1</sup>) ≤ 9, and the average is log(A/M<sup>-1</sup>s<sup>-1</sup>) = 8.6 ± 0.3. For the previously studied alkyl radicals, we had found [4–6] quite narrow frequency ranges. Therefore, we assume that in the present case the large excursions from the average are not significant and are caused by experimental difficulties. For discussion purposes, we recalculated the activation energies from k<sub>296</sub> and the average frequency factor, therefore. Table 3 gives rate data for the addition of PhĊH<sub>2</sub> to 1,2-disubstituted and one trisubstituted alkene, and Table 4 shows the rate constants

Table 3. Absolute Rate Constants<sup>a)</sup> (at 296 ± 1K), Frequency Factor A<sup>a)</sup>, and Activation Energy E<sub>a</sub><sup>a)</sup> for PhĊH<sub>2</sub> Radical Additions to Alkenes (HZC=CXY) in Toluene

Z	X	Y	c [M]	n	k <sub>296</sub> [M <sup>-1</sup> s <sup>-1</sup> ]	log(A/M <sup>-1</sup> s <sup>-1</sup> )	E <sub>a</sub> [kJ/mol]	T [K]
Me	CN	H <sup>b)</sup>	2	30	84(19)	7.6(5)	32.4(60)	273–320
Cl	Cl	Cl	1–3	30	85(20)	6.7(3)	26.8(40)	265–323
CN	CN	H <sup>b)</sup>	0.05–0.15	35	2200(500)	6.3(5)	15.2(50)	261–313

<sup>a)</sup> Standard deviation in units of the last digit is given in brackets.

<sup>b)</sup> (*E*)-Alkene.

Table 4. Absolute Rate Constants<sup>a)</sup> (at 296 ± 1 K), Frequency Factor A<sup>a)</sup>, and Activation Energy E<sub>a</sub><sup>a)</sup> for PhĊMe<sub>2</sub> Radical Additions to Alkenes (H<sub>2</sub>C=CXY) in Toluene

X	Y	c [M]	n	k <sub>296</sub> [M <sup>-1</sup> s <sup>-1</sup> ]	log(A/M <sup>-1</sup> s <sup>-1</sup> )	E <sub>a</sub> [kJ/mol]	T [K]
Z	CO <sub>2</sub> Me	0.15–0.13	7	800(160)	–	–	–
H	Ph	0.1–0.2	10	1200(510)	–	–	–
H	CN	0.075–0.15	10	2200(800)	–	–	–
Me	CO <sub>2</sub> Me	0.05–0.1	30	2700(570)	8.7(5)	29.9(80)	259–314
Ph	Ph	0.05–0.1	9	3800(1400)	–	–	–

<sup>a)</sup> Standard deviation in units of the last digit is given in brackets.

for the addition of PhĊMe<sub>2</sub> to five selected species. In comparison to PhĊH<sub>2</sub>, PhĊMe<sub>2</sub> exhibits a very similar reactivity.

Several groups have hitherto published rate data for the addition of the PhĊH<sub>2</sub> radical to alkenes with which our results can be compared. From a competition with spin trapping, *Gasanov et al.* [16] derived  $k = 5500 \text{ M}^{-1}\text{s}^{-1}$  at room temperature in CH<sub>2</sub>Cl<sub>2</sub> for the addition to methyl acrylate which does not agree with our much lower value of  $k = 430 \text{ M}^{-1}\text{s}^{-1}$  in toluene solution. The trapping technique gives very high rate constants for other radicals as well and may be subject to errors, since additional reactions besides those assumed by the authors [16] may interfere. A better agreement is found with available relative rate constants. For benzene solution at 80°, *Giese and Thoma* [17] report the ratios 4.1:1.3:1.0:0.24:0.048 for (*E*)-ethene-1,2-dicarbonitrile: 1,1-diphenylethene: acrylonitrile: methyl acrylate: prop-1-ene-2-carbonitrile, whereas we find from *Tables 2* and *3* 1.0:1.9:1.0:0.20:0.038 at 296 K. *Premontine and Tirell* [18] obtained (0.33 ± 0.04): 1.0 for the pair styrene: acrylonitrile in CH<sub>2</sub>Cl<sub>2</sub> at room temperature and our value is (0.50 ± 0.14): 1.0. Finally, at 140° in DMF *Terentev et al.* [19] obtained the ratios 0.29:1.0:11.9:24.0 from a telomerization study of alkenes CH<sub>2</sub>=CHX with X = CMe<sub>3</sub>:SiMe<sub>3</sub>:CO<sub>2</sub>Me:CN, and we have 0.55:1.0:13.0:66 for the same series (*Table 2*). In view of the different experimental conditions and methods, the deviations between the data sets are tolerable. Hence, the order of *Table 2* reflects the true reactivity ordering of PhĊH<sub>2</sub> additions.

**3. Analysis and Discussion.** – The ESR parameters of the adduct radical (*Table 1*) agree well with those of similar species [20] and deserve no further comment. Also, the average frequency factor for the addition of PhĊH<sub>2</sub> to CH<sub>2</sub>=CXY (*Table 2*) of  $\log(A/\text{M}^{-1}\text{s}^{-1}) = 8.6 \pm 0.3$  is close to that for the addition of the previously studied primary radicals ĊH<sub>2</sub>OH (8.1 ± 0.1), ĊH<sub>2</sub>CO<sub>2</sub>CMe<sub>3</sub> (8.4 ± 0.1), and ĊH<sub>2</sub>CN (8.7 ± 0.3). This points to the expected similar transition-state structures. We have remarked that the minor differences may even be significant [4c] [6], since they can be related to the barriers of hindered rotation about the radical C<sub>α</sub>–C<sub>β</sub> bonds.

In comparison to other C-centered radicals, for which addition rate constants to the alkenes of *Table 2* are available [4–6], PhĊH<sub>2</sub> shows a rather low reactivity and selectivity. Within one order of magnitude, the rate constants resemble those of Me<sub>2</sub>ĊCN [5], whereas those of ĊH<sub>2</sub>CO<sub>2</sub>CMe<sub>3</sub> and ĊH<sub>2</sub>CN are much larger [6], and those of ĊH<sub>2</sub>OH, Me<sub>2</sub>ĊOH, and Me<sub>3</sub>Ċ cover a much wider range from ca. 100 M<sup>-1</sup>s<sup>-1</sup> to 10<sup>6</sup>–10<sup>7</sup> M<sup>-1</sup>s<sup>-1</sup> [4]. In the analysis of the data for PhĊH<sub>2</sub> of *Table 2*, we now search for polar and enthalpic effects closely following the line of the previous discussions [4–6].

In the literature, different views of the dominating effects have been expressed. *Terentev et al.* [19] and *Minisci et al.* [21] pointed out a nucleophilic behavior of  $\text{Ph}\dot{\text{C}}\text{H}_2$ , and our earlier communications [12] [13] supported this view but ignored a possible enthalpy effect. On the other hand, *Giese* [1] remarked that the large resonance stabilization [22] of  $\text{Ph}\dot{\text{C}}\text{H}_2$  lowers its addition rate constants considerably, and *Tokumura et al.* [23] attributed a difference of addition rates of *p*-substituted benzyls to molecular oxygen to different stabilization energies, *i.e.*, both groups consider enthalpy effects important. Unfortunately, nucleophilic polar and enthalpy effects are not easily separated, because they operate in the same sense for many compounds [3][4-6], and a global analysis [7] did not show a clear distinction, therefore.

Some high-level *ab initio* calculations for the addition of  $\text{Ph}\dot{\text{C}}\text{H}_2$  to ethene are also available [24]. They clearly show that the transition state is later than for other less stabilized radicals, and, hence, lead to the expectation of substantial enthalpy effects.

Figs. 3 and 4 show plots of  $k_{296}/\text{M}^{-1}\text{s}^{-1}$  and activation energies  $E_a^{\text{res}}$  derived from the rate constants with the common frequency factor  $\log(A/\text{M}^{-1}\text{s}^{-1}) = 8.6$  vs. estimated reaction enthalpies  $H_r$  for 17 alkenes. As before,  $H_r$  was calculated from gas-phase heats of formation  $h_f$  and bond dissociation energies *BDE* [4-6] by considering the process



from which one has for the addition of  $\text{R}\cdot$  to the alkene A

$$H_r = h_f(\text{RAH}) - h_f(\text{RH}) - h_f(\text{A}) + \text{BDE}(\text{RAH}) - \text{BDE}(\text{RH}). \quad (5)$$

In particular, we use here the enthalpies for addition of the  $\dot{\text{C}}\text{H}_3$  radical from [4c] and increment for the substitution by  $\text{R} = \text{PhCH}_2$  assuming that *BDE* (RAH) remains unaf-

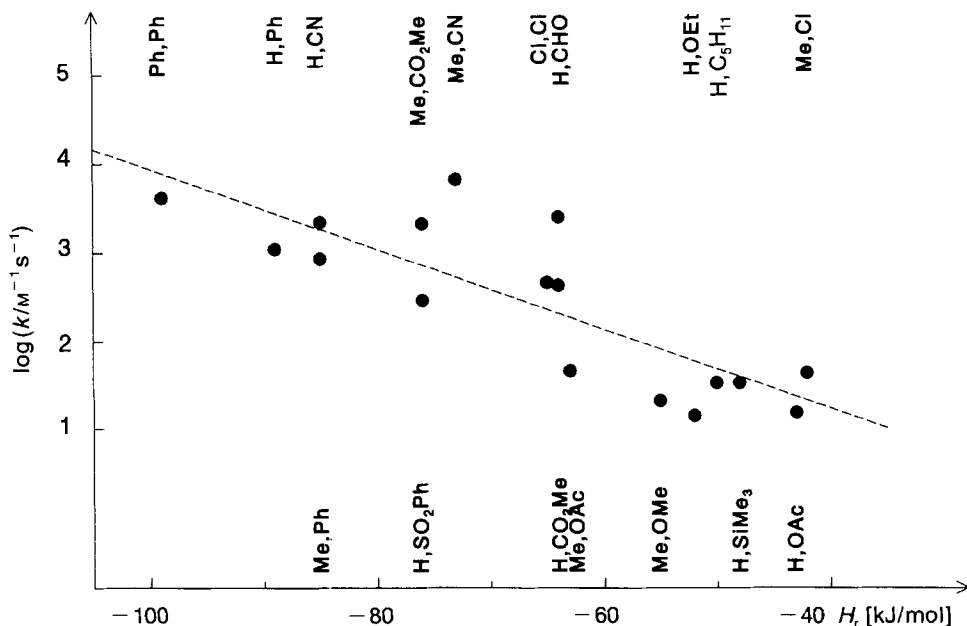


Fig. 3. Rate constants for the addition of  $\text{Ph}\dot{\text{C}}\text{H}_2$  to mono- and 1,1-disubstituted alkenes vs. the reaction enthalpies

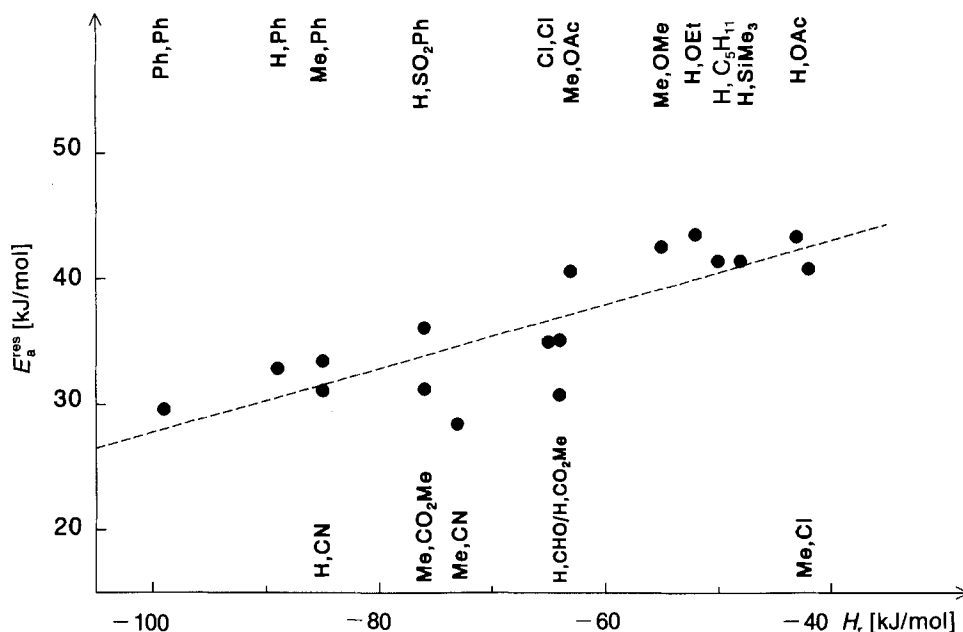


Fig. 4. Activation energies for the addition of  $\text{Ph}\dot{\text{C}}\text{H}_2$  to mono- and 1,1-disubstituted alkenes vs. the reaction enthalpies

fect.  $BDE(\text{PhCH}_2\text{-H}) = 371 \text{ kJ/mol}$  and  $BDE(\text{CH}_3\text{-H}) = 436 \text{ kJ/mol}$  were taken from [25]. The standard reference [11] gives  $h_f(\text{PhCH}_3)$  and  $h_f(\text{CH}_4)$ , and allows an estimate for the difference  $h_f(\text{PhCH}_2\text{AH}) - h_f(\text{CH}_3\text{AH}) = 113 \text{ kJ/mol}$ . These data render the addition of  $\text{Ph}\dot{\text{C}}\text{H}_2$  54 kJ/mol less exothermic than that of  $\dot{\text{C}}\text{H}_3$ . This is due to the radical stabilization. The individual enthalpies are given in Table 5 and may be subject to considerable errors, but the ordering of substances seems reasonable. The linear regressions of Figs. 3 and 4

$$\log(k_{296}/\text{M}^{-1}\text{s}^{-1}) = -(0.57 \pm 0.56) - (0.045 \pm 0.008) H_r [\text{kJ/mol}] \quad (6)$$

$$r = 0.820, 17 \text{ data,}$$

$$E_a^{\text{res}}[\text{kJ/mol}] = (53.2 \pm 3.2) + (0.256 \pm 0.046) H_r [\text{kJ/mol}] \quad (7)$$

$$r = 0.820$$

are significant but worse than for other radicals which previously gave good correlations of  $\log k$  and  $E_a$  with  $H_r$ , namely 2-cyanoprop-2-yl [5]

$$\log(k_{315}/\text{M}^{-1}\text{s}^{-1}) = (0.00 \pm 0.30) - (0.039 \pm 0.004) H_r [\text{kJ/mol}] \quad (8)$$

$$r = 0.922, 19 \text{ data,}$$

cyanomethyl  $\dot{\text{C}}\text{H}_2\text{CN}$  [6]

$$\log(k_{278}/\text{M}^{-1}\text{s}^{-1}) = (1.26 \pm 0.32) - (0.039 \pm 0.004) H_r [\text{kJ/mol}] \quad (9)$$

$$r = 0.931, 20 \text{ data,}$$

and (*tert*-butoxy)carbonylmethyl  $\dot{\text{C}}\text{H}_2\text{CO}_2\text{CMe}_3$  [6]



Table 5. Energy Quantities for Radical Addition to Alkenes ( $H_2C=CXY$ ).  
 $H_r$ ,  $E_a^{res}$  in kJ/mol,  $EA$ ,  $IP$  in eV (from [11] and previous work [4–6]).

Alkenes				Ph $\dot{C}H_2$	
X	Y	EA	IP	$H_r$	$E_a^{res}$
Me	Cl	-1.44	9.76	-42	40.8
H	OCOMe	-1.19	9.19	-43	43.4
H	SiMe <sub>3</sub>	-1.14	9.5	-48	41.4
H	C <sub>5</sub> H <sub>11</sub>	-1.77	9.4	-50	41.4
H	OEt	-2.24	8.8	-52	43.6
Me	OMe	-2.48	8.6	-55	42.6
Me	OCOMe	-1.51	9.10	-63	40.6
H	CO <sub>2</sub> Me	-0.49	9.9	-64	35.1
H	CHO	+0.03	10.10	-64	30.8
Cl	Cl	-0.76	9.79	-65	35.0
Me	CN	-0.17	10.34	-73	28.4
H	SO <sub>2</sub> Ph	~0	10.43	-76	36.1
Me	CO <sub>2</sub> Me	-0.38	9.7	-76	31.2
Me	Ph	-0.23	8.19	-85	33.4
H	CN	-0.21	10.91	-85	31.1
H	Ph	-0.25	8.43	-89	32.8
Ph	Ph	+0.36	8.0	-99	29.6
H	<i>t</i> -Bu	-1.73	9.45	-	42.9
H	Si(OEt) <sub>3</sub>	-1.11	10.06	-	40.7
H	Pyridin-2-yl	-0.41	-	-	30.9

$$\log(k_{296}/M^{-1}s^{-1}) = (2.07 \pm 0.40) - (0.037 \pm 0.004) H_r [\text{kJ/mol}] \quad (10)$$

$$r = 0.894, 20 \text{ data.}$$

However, within the error limits all correlations have the same slopes. Since enthalpy effects are important for the latter three species, we take this as evidence that they are so for Ph $\dot{C}H_2$ . The enthalpy independent terms in *Eqns. 9* and *10* are larger than in *Eqns. 6* and *8* which is due to polar rate enhancements for  $\dot{C}H_2CN$  and  $\dot{C}H_2CO_2CMe_3$  [6]. The global behavior of Ph $\dot{C}H_2$  is similar to that of Me<sub>2</sub> $\dot{C}CN$ , but there are differences in detail which will be discussed later.

Polar effects reflect the admixture of polar states R<sup>+</sup>A<sup>-</sup> and R<sup>-</sup>A<sup>+</sup> to the transition state. For the separated reactants, the energies of these states are given by  $IP(R\cdot) - EA(A)$  and  $IP(A) - EA(R\cdot)$ , respectively, where  $IP$  and  $EA$  are the ionization potentials and electron affinities, respectively. These high energy states are lowered on approach by the *Coulomb* interaction, and thus become able to mix with the unpolar states R·A and R<sup>·3</sup>A [3] [4–6]. Within the frontier-molecular-orbital model this is expressed by stabilizing SOMO-LUMO and SOMO-HOMO interactions. For Ph $\dot{C}H_2$ , one has  $IP(R\cdot)$  of 7.2 eV and  $EA(R\cdot)$  of 0.9 eV [11]. The values for the alkenes are given in *Table 5*. Now, for usual transition-state bond lengths of 210–240 ppm for the new bond a point *Coulomb* attraction of 6 to 6.5 eV seems reasonable, and it has been shown that a final state energy of 1.5–2 eV may cause appreciable polar contributions [3] [4–6]. Very roughly, one then expects that the state R<sup>+</sup>A<sup>-</sup> can be important for all alkenes with  $EA \geq -1.3$  eV and the state R<sup>-</sup>A<sup>+</sup> for alkenes with  $IP \leq 9.3$  eV. For the first compounds a nucleophilic and for the second an electrophilic reactivity pattern would result. However, the estimated *Coulomb* attraction is probably too large here, since in Ph $\dot{C}H_2$  the

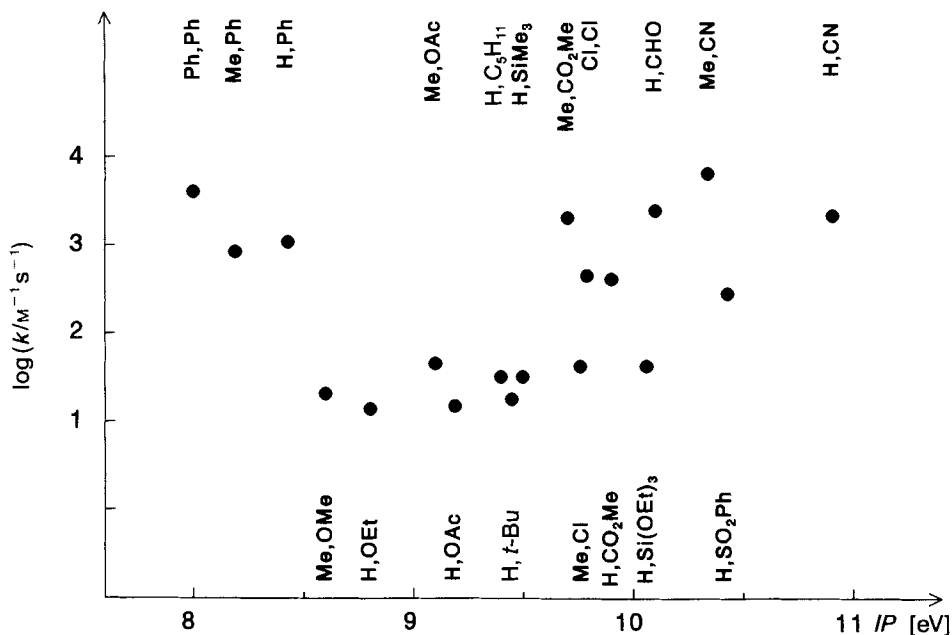


Fig. 5. Rate constants for the addition of  $\text{Ph}\dot{\text{C}}\text{H}_2$  to mono- and 1,1-disubstituted alkenes vs. the alkene ionization potentials

charge is not localized and, therefore, polar effects may be appreciable only for alkenes with higher electron affinities and lower ionization potentials.

In Fig. 5,  $\log(k_{296}/\text{M}^{-1}\text{s}^{-1})$  is plotted vs. the alkene IP. As for other radicals [6], there is a U-shaped behavior which could be called ambiphilic, *i.e.*, electrophilic for alkenes with low IP and nucleophilic for alkenes with high IP and correspondingly high EA. The decrease for low IP is, however, due to the relatively large reactivities of the styrenes. These are more likely due to the high reaction exothermicity, because, for the styrenes, the *Coulomb* interactions are diminished by charge delocalization, and the state mixing is further reduced by low HOMO and LUMO coefficients at the addition site. Hence, with the exception of small effects for the vinyl ethers, we consider electrophilic rate enhancements very unlikely and the U-shape plot insignificant.

Figs. 6 and 7 show the corresponding plots of  $\log(k_{296}/\text{M}^{-1}\text{s}^{-1})$  and  $E_a^{\text{res}}$  vs. the alkene electron affinities. The linear regressions for 20 data

$$\log(k_{296}/\text{M}^{-1}\text{s}^{-1}) = (3.26 \pm 0.15) + (1.03 \pm 0.13) EA [\text{eV}] \quad (11)$$

$$E_a^{\text{res}} [\text{kJ/mol}] = (31.6 \pm 0.8) - (5.8 \pm 0.7) EA [\text{eV}] \quad (12)$$

with  $r = 0.886$  are reasonable, and Eqn. 11 is close to the regression given earlier on the basis of preliminary data [12] [13]. Hence,  $\text{Ph}\dot{\text{C}}\text{H}_2$  expresses a nucleophilic character. However, in comparison to other clearly nucleophilic radicals as 2-hydroxyprop-2-yl [4b].

$$\log(k_{296}/\text{M}^{-1}\text{s}^{-1}) = (6.46 \pm 0.28) + (1.71 \pm 0.19) EA [\text{eV}] \quad (13)$$

$$r = 0.30, 15 \text{ data,}$$

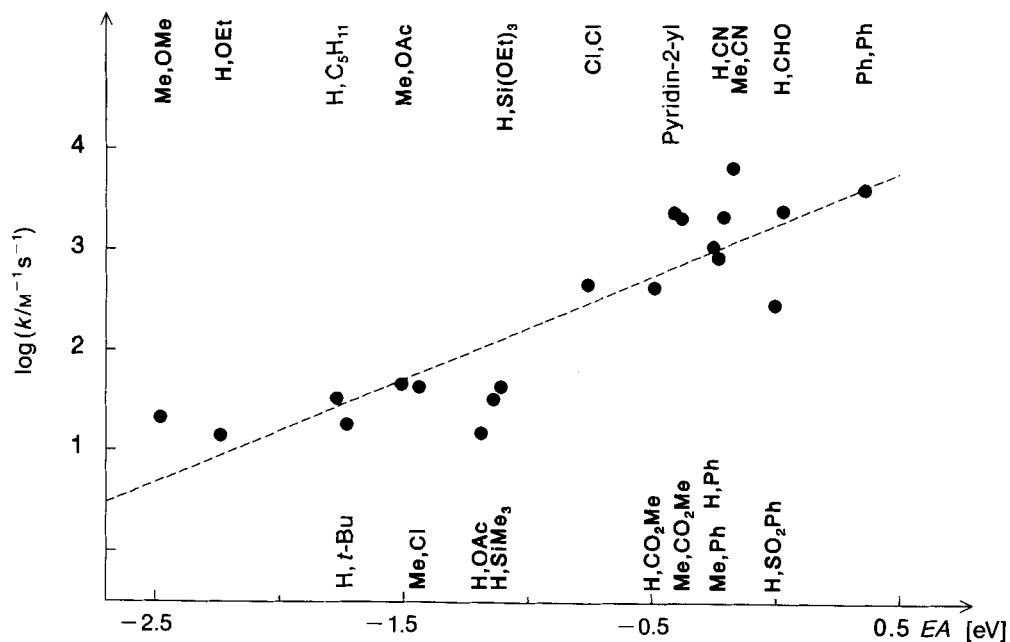


Fig. 6. Rate constants for the addition of  $\text{Ph}\dot{\text{C}}\text{H}_2$  to mono- and 1,1-disubstituted alkenes vs. the alkene electron affinities

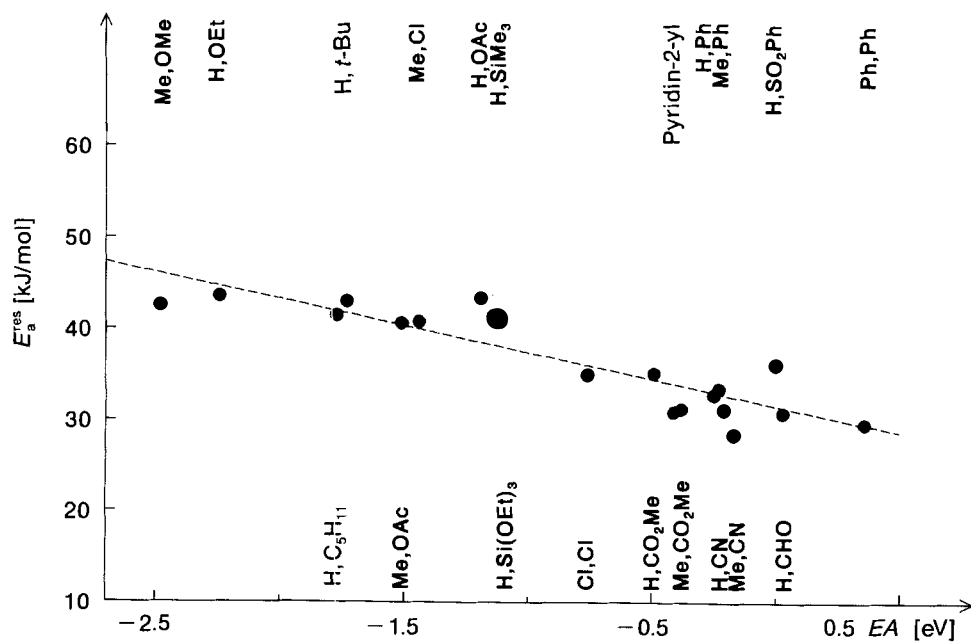


Fig. 7. Activation energies for the addition of  $\text{Ph}\dot{\text{C}}\text{H}_2$  to mono- and 1,1-disubstituted alkenes vs. the alkene electron affinities

$\text{Me}_3\dot{\text{C}}$  [4a]

$$\log(k_{296}/\text{M}^{-1}\text{s}^{-1}) = (6.13 \pm 0.18) + (1.59 \pm 0.13) EA \text{ [eV]} \quad (14)$$

$$r = 0.944, 20 \text{ data,}$$

and  $\dot{\text{C}}\text{H}_2\text{OH}$  [4c]

$$\log(k_{296}/\text{M}^{-1}\text{s}^{-1}) = (5.57 \pm 0.23) + (1.53 \pm 0.17) EA \text{ [eV]} \quad (15)$$

$$r = 0.905, 20 \text{ data,}$$

the correlation is worse. Within this radical series,  $\text{Ph}\dot{\text{C}}\text{H}_2$  is the least nucleophilic species, and the slope of the linear regression (*Eqn. 11*) is less than expected from its *IP* of 7.2 eV [11] which is between those of  $\text{Me}_3\dot{\text{C}}$  (6.7 eV) and  $\dot{\text{C}}\text{H}_2\text{OH}$  (7.56 eV) [4]. Nevertheless, polar effects do operate.

A further separation of enthalpic and nucleophilic polar effects is obtained from a closer inspection of the individual data and a comparison with reactivity patterns of other radicals. In *Figs. 6* and *7*, the rate data do not depend on *EA* for the range  $-2.5 \leq EA \leq -1.0$  eV, and only for alkenes with higher electron affinities  $\log(k/\text{M}^{-1}\text{s}^{-1})$  increases and  $E_a^{\text{res}}$  decreases with increasing *EA*. Earlier [12], this peculiarity escaped our attention, but it is in keeping with *Figs. 3* and *4* where the electron-deficient acrylates, acrylonitriles, and acrolein show the largest deviations from the linear regression. Hence, the overall pattern is that of an enthalpy ordering with a strong nucleophilic polar effect for alkenes with  $EA \geq -1$  eV, except for the styrenes which fall in line with the enthalpy correlation. This is supported by a comparison of the rate constants for five radicals, the styrenes, and some electron-deficient alkenes listed in *Table 6*. For the  $\alpha$ -cyanoalkyl radicals, the enthalpy effects control the variation of the rate constants with alkene substitution and, hence, the largest rate constants are found for the styrenes. On the contrary, for the strongly nucleophilic species  $\dot{\text{C}}\text{H}_2\text{OH}$  and  $\text{Me}_3\dot{\text{C}}$  the reactions of the styrenes are generally slower than the additions to the other alkenes.  $\text{Ph}\dot{\text{C}}\text{H}_2$  is intermediate, and shows large rate constants for styrenes and the strongly electrophilic alkenes. For acrolein and  $\alpha$ -methylacrylonitrile the polar rate enhancement is particularly large, and large polar effects are also required to explain the fast addition to the extremely electron-deficient superalkene  $\text{C}_{60}$  [13].

Our preliminary communication [12] exaggerated the role of polar effects and attributed the large reaction barriers for alkene additions to a special resistance of  $\text{Ph}\dot{\text{C}}\text{H}_2$

Table 6. Selected Rate Constants for the Addition of C-Centered Radicals to Alkenes ( $\text{H}_2\text{C}=\text{CXY}$ ) in  $\text{M}^{-1}\text{s}^{-1}$ . This work and from [4–6] [26].

X	Y	$\text{Ph}\dot{\text{C}}\text{H}_2$ (296 K)	$\text{Me}_2\dot{\text{C}}\text{CN}$ (315 K)	$\dot{\text{C}}\text{H}_2\text{CN}$ (278 K)	$\dot{\text{C}}\text{H}_2\text{OH}$ (296 K)	$\text{Me}_3\dot{\text{C}}$ (300 K)
H	$\text{CO}_2\text{Me}$	430	367	110000	710000	1100000
Me	Ph	850	2310	660000	28000	60000
H	Ph	1100	2410	380000	23000	132000
Me	$\text{CO}_2\text{Me}$	2100	1590	240000	600000	660000
H	CN	2200	2200	110000	1100000	2000000
H	CHO	2500	1200	25000	2100000	2800000
Ph	Ph	4100	7010	2400000	140000	1000000
Me	CN	6600	1060	170000	670000	1700000

against deformation in the transition state. This has correctly been criticized [24], but the reported calculation of the barrier for the addition to ethene did show a large contribution of the radical deformation energy due to the lateness of the transition state. We were unable to measure the rate constant for the addition to ethene, because the necessary high alkene concentrations could not be reached. However, in the same way as for the other alkenes, we estimate the reaction enthalpy for this addition as  $H_r = -44$  kJ/mol and then predict via Eqns. 6 and 7  $E_a = 42$  kJ/mol and  $k_{296} = 26 \text{ M}^{-1}\text{s}^{-1}$ . The calculations [24] gave  $H_r$  and  $E_a$  as 1.2 kJ/mol and 79 kJ/mol (UHF/6-31G\*),  $-154$  kJ/mol and 69 kJ/mol (UMP 2/6-31G\*), and  $-64$  kJ/mol and 33.5 kJ/mol (PMP 2/6-31G\*), respectively. In [12], we also presented room-temperature data for the addition of *p*-X-substituted  $\text{Ph}\dot{\text{C}}\text{H}_2$  radicals ( $X = \text{OMe}, \text{Me}, \text{F}, \text{CN}$ ) to selected alkenes. They varied little with radical substitution, though this shifts the radical *IP* from 6.3 ( $X = \text{OMe}$ ) to 7.9 eV ( $X = \text{CN}$ ). Actually, these findings indirectly support large enthalpy and lower polar effects, since the radical stabilization is only moderately varied by the substituents [27]. The reactivity of *p*-X- $\text{C}_6\text{H}_4\dot{\text{C}}\text{H}_2$  towards ethoxyethene [12] also points to a slight electrophilicity for the additions to very electron-rich alkenes as noted above and in [7].

For  $\text{Ph}\dot{\text{C}}\text{Me}_2$ , we obtained only a few rate constants for the addition to selected and rather reactive alkenes (Table 5). Hence, we cannot perform a detailed analysis. Grossly,  $\text{Ph}\dot{\text{C}}\text{Me}_2$  reacts as fast as  $\text{Ph}\dot{\text{C}}\text{H}_2$ . A rough estimate predicts that the exothermicity is by 16 kJ/mol lower, and via Eqns. 6, 8, 9, and 10 this leads to a decrease of  $\log k$  by a factor of 5. On the other hand, the *IP* of  $\text{Ph}\dot{\text{C}}\text{Me}_2$  (6.6 eV [11]) is lower than that of  $\text{Ph}\dot{\text{C}}\text{H}_2$  (7.2 eV [11]), and this can cause larger nucleophilic rate enhancements. Both effects may cancel each other, and this would explain the very similar reactivity. As pointed out in [4],  $\alpha$ -methylation of a radical has little retarding effect. The frequency factor for the  $\text{Ph}\dot{\text{C}}\text{Me}_2$  addition to methyl methacrylate of  $\log (A/\text{M}^{-1}\text{s}^{-1}) = 8.7 \pm 0.5$  is substantially larger than our previous values for other  $\text{X}\dot{\text{C}}\text{Me}_2$  radicals of 7.5 ( $X = \text{Me}$ , average for many alkenes [4]), 6.4 ( $X = \text{OH}$ , 3.3, dimethylbut-1-ene [4]), and 7.7 ( $X = \text{CN}$ , styrene [5]), and it is also larger than for some  $\text{X}\dot{\text{C}}\text{H}_2$  radicals. Since  $\text{X}\dot{\text{C}}\text{Me}_2$  radicals should encounter some additional loss of entropy by a hindrance of Me-group rotation in the transition state, our value for  $\text{Ph}\dot{\text{C}}\text{Me}_2$  may be too high and is probably affected by the experimental difficulties mentioned in Sect. 2 of this work.

**4. Relations to Chain-Propagation Constants in the Homo- and Copolymerization of Styrene.** – The rate constant of the addition step in free radical polymerization largely determines the polymer composition and properties, and, hence, numerous studies have been performed [28]. Yet, the reliability of the methods and results are a matter of constant debate [29], because direct measurements are rare. The determination of absolute or relative rate constants for low-molecular-weight radicals avoids some of the problems encountered with polymer systems, and these can serve as model for many cases [1] [18]. In fact, we have shown earlier that ratios of absolute rate constants for the addition of  $\dot{\text{C}}\text{H}_2\text{CN}$  and  $\dot{\text{C}}\text{H}_2\text{CO}_2\text{CMe}_3$  agree very well with the copolymerization parameters  $r_1$  of acrylonitrile and alkyl acrylate [6]. Here, we compare rate data of the growing chain radical of styrene, polystyryl  $\text{RCH}_2\dot{\text{C}}\text{HPh}$ , with our results for  $\text{Ph}\dot{\text{C}}\text{H}_2$  and  $\text{Ph}\dot{\text{C}}\text{Me}_2$ . This comparison is especially justified by the equal reactivities of the primary  $\text{Ph}\dot{\text{C}}\text{H}_2$  and the tertiary  $\text{Ph}\dot{\text{C}}\text{Me}_2$  radical which suggest similar values for the secondary polystyryl species.

The most recent *Arrhenius* parameters for the homopolymerization rate constant of styrene in bulk center around  $\log (A/M^{-1}s^{-1}) = 7.1$  and  $E_a = 30$  kJ/mol [30]. From our data, one derives  $E_a = (31 \pm 2)$  kJ/mol (*Tables 2 and 5*) and  $7.5 \leq \log (A/M^{-1}s^{-1}) \leq 8$ , *i.e.*, between  $\log (A/M^{-1}s^{-1}) \geq 8$  for the primary and  $\log (A/M^{-1}s^{-1}) \leq 7.5$  for the tertiary radicals. The agreement is very satisfactory, and the lower frequency factor of polystyryl is not unexpected in view of the conformational complexity of the propagating species. *Fig. 8* shows the ratios  $r_1^{\text{calc}}$  of the rate constants of the addition of  $\text{Ph}\dot{\text{C}}\text{H}_2$  to styrene and to other alkenes derived from *Tables 2 and 3* plotted vs. the experimental copolymerization parameter  $r_1^{\text{exp}}$  for the polystyryl radical. For the latter quantity, the most recent values were selected from [28]. Based on 18 data, the correlation

$$\log(r_1^{\text{calc}}) = (0.06 \pm 0.08) + (1.00 \pm 0.08) \log(r_1^{\text{exp}}) \quad (16)$$

is excellent ( $r = 0.948$ ), and this ensures that rate constants for small radicals can be used to predict copolymerization parameters. *Table 2* contains alkenes  $\text{CH}_2=\text{CXY}$  for which the styrene copolymerization parameter  $r_1 = k(\text{styrene})/k(\text{alkene})$  are not yet available, our data predict  $r_1 = 61$  for X, Y = H, CMe<sub>3</sub>,  $r_1 = 52$  for Me, OMe,  $r_1 = 33$  for H, pentyl, and  $r_1 = 24$  for Me, OAc.

In summary, the addition of  $\text{Ph}\dot{\text{C}}\text{H}_2$  and other benzylic radicals to alkenes is irreversible, but the exothermicity is low. This causes a late transition state and rather high reaction barriers which vary with alkene substitution according to the variation of the exothermicity. For strongly electron-deficient alkenes and C<sub>60</sub>, partial electron-transfer interactions lower the barriers so that  $\text{Ph}\dot{\text{C}}\text{H}_2$  radicals become markedly nucleophilic. For vinyl ethers, a weak electrophilic rate enhancement is also noticed.

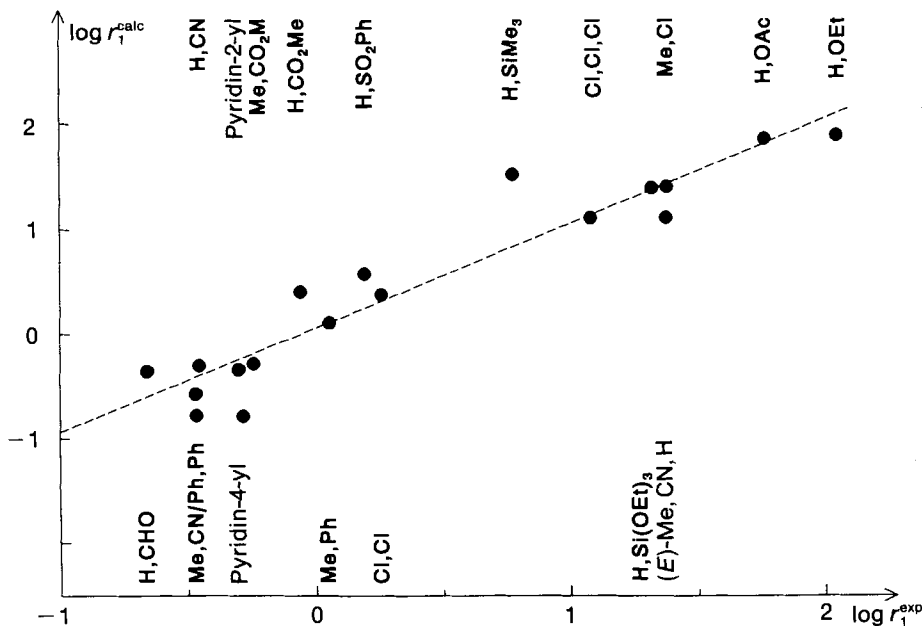


Fig. 8. Correlation of relative rate constants for the addition of  $\text{Ph}\dot{\text{C}}\text{H}_2$  to alkenes with the copolymerization parameter  $r_1$  of styrene

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