Absolute Rate Constants for the Addition of Hydroxymethyl Radicals to Alkenes in Methanol Solution

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Abstract

Absolute rate constants and their temperature dependencies were determined for the addition of hydroxymethyl radicals ($\dot{C}H_2OH$) to 20 mono- or 1,1-disubstituted alkenes ($CH_2 = CXY$) in methanol by time-resolved electron spin resonance spectroscopy. With the alkene substituents the rate constants at 298 K (k_{298}) vary from 180 M⁻¹s⁻¹ (ethyl vinylether) to 2.1 \cdot 10⁶ M⁻¹s⁻¹ (acrolein). The frequency factors obey log $A/M^{-1}s^{-1} = 8.1 \pm 0.1$, whereas the activation energies (E_a) range from 11.6 kJ/mol (methacrylonitrile) to 35.7 kJ/mol (ethyl vinylether). As shown by good correlations with the alkene electron affinities (EA), log $k_{298}/M^{-1}s^{-1} = 5.57 + 1.53 \cdot EA/eV$ (R² = 0.820) and $E_a = 15.86 - 7.38 \cdot EA/eV$ (R² = 0.773), hydroxymethyl is a nucleophilic radical, and its addition rates are strongly influenced by polar effects. No apparent correlation was found between E_a or log k_{298} with the overall reaction enthalpy. (© 1995 John Wiley & Sons, Inc.

Introduction

The addition of carbon centered radical to alkenes is one of the most important free radical reactions and is widely used in polymer chemistry and in organic synthesis. Therefore, the factors which govern the addition rate constants have been discussed extensively [1]. They involve an interplay of polar, steric, and enthalpy effects of the radical and the alkene substituents which is difficult to disentangle. To provide a larger basis for a separation of these factors we have previously presented series of absolute rate data obtained by time-resolved electron spin resonance for the addition of tert-butyl $(CH_3)_3\dot{C}$ [2(a)], 2-hydroxy-2-propyl $(CH_3)_2\dot{C}OH$ [2(b)], 2-cyano-2-propyl $(CH_3)_2\dot{C}CN$ [2(c)], benzyl $C_6H_5\dot{C}H_2$ [2(d)], and tert-butoxycarbonylmethyl $(CH_3)_3COOC\dot{C}H_2$ [2(e)] radicals to a variety of mono- and 1,1-disubstituted alkenes in liquid solutions. For tert-butyl and 2-hydroxy-2-propyl a high nucleophilicity and a dominance of polar alkene substituent effects were established, while the addition rates for 2-cyano-2-pyopyl were found to be controlled by the total reaction enthalpy. The other two radicals displayed influences of both polar and enthalpy effects.

Here, we report rate constants and Arrhenius parameters for the addition of the hydroxymethyl radical CH_2OH to 20 alkenes in methanol solution. The radical is well known to be nucleophilic [3,4] so that strong polar alkene substituent effects are expected. On the other hand, its ionization potential (7.56 eV [5]) is between those of the very nucleophilic species ((CH_3)₃C, 6.7 eV; (CH_3)₂COH, 6.48 eV) and (CH_3)₂CCN (8.2 eV) so that the polar effects should be weaker than observed for

the former, and reaction enthalpy effects could become noticeable as in the case of the latter species. The radical was also chosen because Radom et al. [6(c)] have recently carried out thorough ab initio calculations of the reaction enthalpy and of the barrier for addition to several alkenes so that experimental and theoretical results can be compared.

As radical source we use the photolysis of di-tert-butylperoxide in the solvent methanol in which $\dot{C}H_2OH$ is formed by the fast hydrogen transfer to the primary tert-butoxy species. To ensure the validity of the reaction mechanism we also present data on the self-termination kinetics of $\dot{C}H_2OH$ and on the structure of its alkene adducts.

Experimental and Results

The arrangements and procedures for steady-state and time-resolved electron spin resonance have been described in detail in earlier work [2]. Oxygen free solutions of di-tert-butyl-peroxide (1.09M) in methanol containing appropriate amounts of alkenes were photolyzed (260 nm $\leq \lambda \leq 340$ nm) while slowly flowing through a flat quartz reaction cell of 0.4 mm thickness inside the ESR cavity and were thermostatted by a surrounding nitrogen gas stream. The solution flow rates were chosen high enough (0.33–6.3 ml/min) so that the spectrum amplitudes became independent on the flow-rate. This indicates negligible substrate depletion. To achieve this condition for highly reactive alkenes the photolysis intensity was reduced by the insertion of grids, diaphragms, and additional cut-off filters. Methanol (p.a.) was obtained from Aldrich and was employed without further purification. Ditert-butylperoxide (Fluka, Aldrich) and the alkenes were purified by distillation before use.



Figure 1. ESR-spectra of radicals during photolysis of di-tert-butylperoxide in methanol, (a) in the absence of alkenes and (b) in the presence of 0.11 M methylacrylate.

Steady-state ESR-spectra taken during photolysis of di-tert-butylperoxide in the absence of alkenes revealed the formation of hydroxymethyl $\dot{C}H_2OH$ as the only detectable radical as shown in Figure 1(a) $(2H_{\alpha} = 17.35 \text{ G}, \text{ H}(OH) = 1.15 \text{ G}, \text{ and } \text{g} = 2.0032 \text{ at } 298 \text{ K}$). This reflects the reaction mechanism

(1)
$$(CH_3)_3COOC(CH_3)_3 \xrightarrow{h\nu} 2(CH_3)_3CO$$

(2)
$$(CH_3)_3C\dot{O} + HOCH_3 \xrightarrow{h_H} (CH_3)_3COH + HO\dot{C}H_2$$

(3)
$$2\text{HOCH}_2 \xrightarrow{2k_i^{\mathsf{M}}} \text{termination products.}$$

The high rate constant for the hydrogen transfer (2) $(k_{\rm H} = 3.4 \cdot 10^5 \text{ M}^{-1} \text{s}^{-1} \text{ at } 298 \text{ K}$ [7]) limits the lifetime of tert-butoxy to the submicrosecond region and precludes the formation of methyl radicals via the much slower β -fragmentation (4) [8].

(4)
$$(CH_3)_3 \dot{CO} \xrightarrow{k_\beta} (CH_3)_2 CO + \dot{C}H_3$$

Figure 2 shows a kinetic trace (a) for CH₂OH at 298 K in an alkene free solution. It exhibits a perfect second-order decay with a lifetime $\tau = 631 \ \mu$ s, as expected if (1)–(3) are the only relevant reactions. Absolute rate constants $2k_t^{\rm M}$ for the self-termination reaction (3) were obtained from the second-order lifetimes for 252 K $\leq T \leq 312$ K via standard procedures [9] using $2k_t$ for tert-butyl radicals at 298 K ($3.3 \cdot 10^9 \ {\rm M}^{-1}{\rm s}^{-1}$ [9]) for calibration purposes. This lead to the Arrhenius parameters $A_t^{\rm M} = (4.8 \pm 0.9) \cdot 10^{11} \ {\rm M}^{-1}{\rm s}^{-1}$ and $E_{\rm at}^{\rm M} = (11.1 \pm 0.5) \ {\rm kJ/mol}$ which agree with previous literature data [7(b),10], and confirm that the self-termination is diffusion controlled.

With alkenes present, CH_2OH was partially replaced in the steady-state spectra by secondary radicals with spectral features confirming the general structure



Figure 2. [CH₂OH] vs. time (a) in the absence of alkenes with pure second-order kinetics and (b) in the presence of 0.18 M isopropenyl acetate with a mixed first- and second-order kinetics. Bottom traces are residuals of fits to eq. (8).

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HOCH₂CH₂CXY. An example is given in Figure 1(b) for mehtylacrylate (X = H, Y = COOCH₃). The additional lines are due to HOCH₂CH₂CHCOOCH₃ with H_{α} = 20.40 G, 2H_{β} = 22.32 G, 3H(CH₃) = 1.4 G and g = 2.0035. The ESR parameters of all adduct radicals observed in this study are collected in Table I. They are in good agreement with earlier data for the same or similar species [11]. Secondary radicals produced by the possible hydrogen abstraction from alkenes such as acrolein could not be detected. Also absent were radicals of type HOCH₂CXYCH₂ which ensures that addition of CH₂OH occurs nearly exclusively at the unsubstituted alkene carbon. From these observations it is obvious that the presence of alkenes A leads to the additional reactions:

$$\dot{\mathrm{CH}}_{2}\mathrm{OH} + A \xrightarrow{k_{a}} \dot{A}$$

$$\dot{\mathrm{CH}}_{2}\mathrm{OH} + \dot{A} \xrightarrow{k_{x}} P_{x}$$

(7)
$$2\dot{A} \xrightarrow{k_i^A} P_A$$

where \dot{A} denotes the adduct radicals, and reaction (6) and (7) represent their crossand self-terminations.

To obtain the rate constants for the addition (5) time-resolved experiments were performed on one of the center ESR-lines of $\dot{C}H_2OH$ under conditions of low alkene concentrations for which the pseudo-first-order addition process is a slight perturbation of the second order self-termination (3), only. As has been shown and utilized earlier [2] the decay of $\dot{C}H_2OH$ is then described by

(8)
$$[\dot{C}H_2OH] = [\dot{C}H_2OH]_0 \cdot \exp(-t/\tau_1) \cdot (1 + t/\tau_2)^{-1}$$

where $\tau_1 = (k_a \cdot [A])^{-1}$ and $\tau_2 = (2k_t[R]_0)^{-1}$. $[R]_0$ is the total radical concentration at the on-set of the decay. Equation (8) is exact if $2k_t^M = k_x = 2k_t^A$ holds and is otherwise a good approximation for $\tau_1/\tau_2 \ge 5$, i.e., dominant second-order decay. Figure 2(b) shows a kinetic trace for 0.18 M isopropenyl acetate and a fit to eq. (8) which lead to $\tau_1 = 8.59$ ms and $\tau_2 = 672 \ \mu$ s. For each alkene the pseudo-first-order lifetimes were measured for several concentrations. Figure 3 shows τ_1^{-1} vs. concentration [A] for two alkenes, and the individual data represent averages from 3–6 kinetic runs. The rate constants follow from the slopes of the straight lines drawn through the data points.

Alkene	Adduct	g	Coupling Constants (G)
$CH_2 = CHSO_2C_6H_5$	RCH2CHSO2C6H5	2.0024	$H_{\alpha}: 20.8, 2H_{\beta}: 23.8$
$CH_2 = CMeCN$	RCH ₂ CMeCN	2.0028	$2H_{\beta}$: 17.78, $3H_{\beta}$: 21.08, ¹⁴ N : 3.38
$CH_2 = CHCN$	RCH2CHCN	2.0030	$H_{\alpha}: 20.27, 2H_{\beta}: 21.8, {}^{14}N: 3.47$
$CH_2 = CMeCO_2Me$	RCH ₂ ĊMeCO ₂ Me	2.0030	$2H_{\beta}$: 14.28, $3H_{\beta}$: 22.1, $3H(OMe)$: 1.3
$CH_2 = CHCO_2Me$	RCH2CHCO2Me	2.0035	H_{α} : 20.40, $2H_{\beta}$: 22.33, $3H(OMe)$: 1.4
$CH_2 = CCl_2$	$RCH_2\dot{C}Cl_2$	2.0077	$2H_{\beta}$: 11.49, 2^{35} Cl: 3.3
$CH_2 = CHSi(OEt)_3$	RCH2CHSi(OEt)3	2.0027	$H_{\alpha}: 20.2, 2H_{\beta}: 25.0$
$CHMe = CCl_2$	RCHMeCCl ₂	2.0073	H_{β} : 7.7, 2 ³⁵ Cl: 4.1
$CH_2 = CHOCOMe$	RCH ₂ ĊHOCOMe	2.0028	H_{α} : 17.0, 2H _{\beta} : 20.0, 3H(OMe): 1.3, 2H _{\gamma} : 0.7
$CH_2 = CHC(Me)_3$	RCH ₂ CHC(Me) ₃	2.0027	H_{α} : 26.0, $2H_{\beta}$: 21.0, $9H(Me)$: 0.65
$CH_2 = CHCHO$	RCH ₂ CHCHO	2.0044	H_{α} : 18.2, $2H_{\beta}$: 19.36, $H_{\beta}(CHO)$: 1.34

TABLE I. ESR-parameters of adduct radicals in methanol at or close to 298 K ($R = CH_2OH$).



Figure 3. Pseudo-first-order plot for the addition of $\dot{C}H_2OH$ to styrene and to vinylacetate at 298 K.

Experiments at different temperatures then gave their Arrhenius parameters (Fig. 4). Table II shows the results for the 20 alkenes of type $CH_2 = CXY$ employed in this work together with the temperature and concentration ranges. Errors are quoted in units of the last digit given for the data. On variation of the alkene substituents the rate constants at room temperature change from 180 M⁻¹s⁻¹ to 2.1 \cdot 10⁶ M⁻¹s⁻¹, i.e., by about 4 orders of magnitude. The frequency factors fall within about one order of magnitude with an average log $A/M^{-1}s^{-1} = 8.1 \pm 0.1$. Hence, the variation of the rate constants is mainly due to the changing activation energies.

By a rather indirect technique Myshkin et al. [12] have previously obtained $k_{453} = 630 \text{ M}^{-1}\text{s}^{-1}$ for the addition to ethene and estimated log $A/M^{-1}\text{s}^{-1} = 4.5$ and $E_a = 14.6 \text{ kJ/mol}$. In comparison with our data (Table II) the rate constant is of the expected order of magnitude while the activation parameters show serious disagreement. Buxton et al. [13] found $k_{300} = 2.6 \cdot 10^7 \text{ M}^{-1}\text{s}^{-1}$ for the addition to acrylamide in aqueous solution which is at the upper limit of our experimental capabilities. In their recent ab initio calculations on the addition of $\dot{C}H_2OH$ to alkenes Radom et al. [6(c)] obtained barriers at 0 K for ethene (32.7 kJ/mol), vinylchloride (24.6 kJ/mol), acrolein (18.3 kJ/mol), and acrylonitrile (11.7 kJ/mol). With the exception of acrolein, where we find a lower activation energy, their data agree with the experimental findings (Table II) within the experimental errors.

Discussion

The frequency factor for the addition does not vary systematically with alkene substitution as also found earlier for other radical additions to the same alkenes [2,14]. Its average $\log A/M^{-1}s^{-1} = 8.1 \pm 0.1$ is close to the corresponding averages



Figure 4. Rate constants for the addition of CH_2OH to α -methylstyrene and to vinyltrimethylsilane at various temperatures and fits the Arrhenius law.

Χ, Υ	T[K]	$c[\mathbf{M}]$	$k_{298} [\mathrm{M}^{-1} \; \mathrm{s}^{-1}]$	$\log[A/M^{-1} s^{-1}]$	Ea[kJ/mol]
H, OEt	261-311	0.41-0.82	180(20) ^a	8.3(10) ^b	35.7(120) ^b
Me, OMe	260 - 312	0.61/1.0	230(20)	8.1(4)	33.0(9)
Me, Me	271 - 311	0.25/0.33	240(40)	8.0(2)	31.9(10)
H, Me	259 - 304	0.12/0.31	270(50)	7.5(5)	28.7(30)
H, Et	260 - 311	0.14/0.27	300(50)	7.5(3)	28.9(17)
Н, Н	271 - 306	0.063/0.077	410(70) ^c	7.9(9) ^c	30.4(72)
H, OCOMe	251 - 320	0.086 - 0.32	590(50)	7.7(4)	27.6(28)
Me, OCOMe	246 - 310	0.18/0.36	680(50)	7.4(6)	26.4(36)
H, SiMe ₃	242 - 318	0.067/0.094	2060(200)	7.8(3)	25.7(9)
Me, Cl	256 - 312	0.05/0.06	2110(400)	7.9(3)	25.9(18)
H, Cl	245 - 311	0.026/0.1	5000(900)	8.2(6)	26.0(20)
H, C ₆ H ₅	238 - 301	12-26 mM	$2.3 \cdot 10^4 (2 \cdot 10^3)$	8.4(3)	22.1(4)
Me, C_6H_5	237 - 309	10/15 mM	$2.8 \cdot 10^4 (2 \cdot 10^3)$	8.6(4)	25.2(21)
Cl, Cl	232 - 298	12/25 mM	$5.3 \cdot 10^4 (10^3)$	8.1(8)	19.3(39)
$C_{6}H_{5}, C_{6}H_{5}$	255 - 313	0.15-1.5 mM	$1.4 \cdot 10^5 (10^4)$	8.3(4)	18.3(24)
Me, CO ₂ Me	244 - 299	0.4/0.7 mM	$6.0 \cdot 10^5 (5 \cdot 10^4)$	8.6(4)	17.8(24)
Me, CN	234 - 299	0.4/2 mM	$6.7 \cdot 10^5 (6 \cdot 10^4)$	8.2(4)	11.6(5)
H, CO ₂ Me	238 - 298	0.4/1.0 mM	$7.1 \cdot 10^5 (6 \cdot 10^4)$	8.7(4)	14.4(8)
H, CN	234 - 299	0.1 - 0.5 mM	$1.1 \cdot 10^{6} (10^{5})$	8.3(2)	13.2(10)
H, CHO	254 - 299	0.16-0.4 mM	$2.1\cdot10^6(3\cdot10^5)$	8.4(5)	12.0(25)

TABLE II. Rate data for the addition of \cdot CH₂OH radicals to alkenes CH₂ = CXY in methanol.

^a Standard deviation in brackets.

^b Standard deviation in units of the last digital number given in brackets.

^c Statistically corrected.

for tert-butyl (7.5 \pm 1.0), tert-butoxycarbonylmetyl (8.4 \pm 0.1) and benzyl (8.9 \pm 1.0). This supports a similarity of the transition state structures which is known from theoretical work [6,15]: While the newly forming bond is still long (210-240 pm)the angle of attack is already tightly prescribed, and there is a considerable outof-plane deformation at the two newly bonded carbon atoms. Here, the differences of our average frequency factors may be significant because they can be rationalized in terms of these transition states features and known radical properties: The exothermicity of the addition is expected to decrease in the order $(CH_3)_3C \approx HOCH_2 >$ $(CH_3)_3COOCH_2 > C_6H_5CH_2$, and consequently the transition state becomes later in this series. This should lead to an increasing pyramidalization of the radical centers. Now, the three primary radicals have partial $R-CH_2$ double bonds, and the barriers to rotation about these bonds increase as $HOCH_2 < (CH_3)_3COOCCH_2 < C_6H_5CH_2$ [16]. In the transition state these barriers will be smaller, and the largest effect is expected for the latest transition state. Hence, the primary radical gain motional entropy in the order $HOCH_2 < (CH_3)_3COOCCH_2 < C_6H_5CH_2$, and this corresponds to the order of the frequency factors. The lower value of the tertiary species $(CH_3)_3C$ which also holds for $(CH_3)_2COH$ and $(CH_3)_2CCN$ [2(b),(c)] is also reasonable since these radicals will experience increased CH₃-group interactions upon pyramidalization, i.e., more hindered internal motions.

In the discussion of the activation energies we will now follow the lines of ref. [2(c)] and [6(c)] and seek correlations with reaction enthalpies and, for the polar effects, with ionization potentials and electron affinities. Steric effects are ignored since they should be small for the exclusive additions at the unsubstituted carbon atom of the alkenes as observed here, and since an inspection of the data in Table II does not reveal obvious trends.

The overall enthalpy change in the addition reaction (5) is estimated by considering the reaction sequence

(9)
$$\mathbf{R} - \mathbf{H} + \mathbf{A} \longrightarrow \dot{\mathbf{R}} + \dot{\mathbf{H}} + \mathbf{A} \longrightarrow \dot{\mathbf{H}} + \dot{\mathbf{A}} \longrightarrow \mathbf{A} - \mathbf{H}$$

from which one has

(10)
$$H_r = h_f(A - H) - h_f(R - H) - h_f(A) + BDE(A - H) - BDE(R - H).$$

Experimental data for the enthalpies of formation and bond dissociation energies appearing on the r.h.s. of eq. (10) determined at or close to standard conditions are applied, and deviations from ideality, e.g., solvent effects, are ignored. Since the enthalpies of formations are known for many species A - H with $R = CH_3$ but not for $R = CH_2OH$ we first determine H_r for the addition of the methyl radical CH₃ and then increment for the substitution. The bond dissociation energies BDE(A - H)were adopted from related compounds and from the most recent literature known to us. Because of changes of these sources they differ in part slightly from our earlier estimates [2(c)]. Table III gives $h_f(A)$, $h_f(A - H)$, BDE(A - H) and the reaction enthalpies for the addition of CH_3 and of CH_2OH , and refers to the estimation procedures and the literature. In addition BDE (CH₃—H) = 436 kJ/mol [18], h_f (CH₄) = -74.5 kJ/mol [5] were applied, and from the enthalpies of various pairs of type CH_3 — $CXYZ/HOCH_2$ —CXYZ a change of $h_f(A - H)$ of -150 kJ/mol was deduced for the substitution of CH_3 by CH_2OH . These data also imply that the addition of CH_2OH is an average 11.5 kJ/mol less exothermic than that of CH_3 . In view of the still existing uncertainties of many bond dissociation energies and of the estimation procedures the reaction enthalpies given in Table III cannot be very precise and errors of up to about 10 kJ/mol could occur. However, there is a rather good agreement with Radom's theoretical results [6] which are given in brackets in the Table both for the additions of $\dot{C}H_3$ and $\dot{C}H_2OH$. This supports the consistency of the estimations.

Х, Ү	$h_{\rm f}(A)$	$h_{\rm f}(A-{ m H})$	BDE(A-H)	$H_r(CH_3) \\$	$H_r(CH_2OH) \\$	EA(A)	IP(A)
H, OEt	-141	-272.2	387 ^g	106	-94.5	-2.24	8.8
Me, OMe	-187^{b}	-312	378^{h}	109	-97.5	-2.48	8.64
Me, Me	-16.9	-153.8	398^{i}	-100	-88.5	-2.19	9.6
H, Me	20.2	-126.5	404 ⁱ	-104	-92.5	-1.99	9.5
H, Et	-0.4	-146.5	404 ⁱ	-104	-92.5	-1.90	9.59
H, H	52.2	-104.5	420^{i}	-98	-86.5	-1.78	10.51
				(-93.5)	(-87.1)		
H, OCOMe	-314.9	-454	404 ^j	-97	-85.5	-1.19	9.19
Me, OCOMe	-349	-501	396 ^j	-117	-105.5	-1.51	9.1
H, SiMe ₃	-123	-263^{c}	400^{k}	-102	-90.5	-1.14	9.5
Me, Cl	-21	-161	406 ¹	-96	-84.5	-1.44	9.76
H, Cl	23	-132.4	411 ^m	-106	-94.5	-1.28	10.0
				(-105.9)	(-97.8)		
H, C_6H_5	147.7	8	358^{n}	-143	-131.5	-0.25	8.43
Me, C ₆ H ₅	113	-17.3	353 ⁿ	-139	-127.5	-0.23	8.19
Cl, Cl	2.3	-149^{d}	394°	-119	-107.5	-0.76	9.79
$C_{6}H_{5}, C_{6}H_{5}$	246	115^{e}	339^{p}	-153	-141.5	+0.36	8.0
Me, CO ₂ Me	-348	-492	$375^{ m q}$	-130	-118.5	-0.38	9.7
Me, CN	130	3^{f}	362^{r}	-127	-115.5	-0.17	10.35
H, CO ₂ Me	-312	-452	383^{q}	-118	-106.5	-0.49	9.9
H, CN	184	31	376^{r}	-139	-127.5	-0.21	10.95
				(-129.3)	(-123.7)		
H, CHO	-77	-207.5	$374^{\rm s}$	-118	-106.5	(+0.03)	10.1
				(-120.7)	(-118.6)		

TABLE III. Energy quantities for alkenes and addition products at or close to 298 K. h_f , BDE and H_r in kJ/mol, EA and IP in eV^a. Values in brackets from ref. [6c].

^a Unless quoted otherwise standard enthalpies of formation, electron affinities, and ionization potentials are taken from refs. [5,17] and references cited in previous work [2].

^b From $h_f^0(H, OEt)$ and $\Delta h_f^0(CH_2CHOMe/CH_2C(CH_3)OMe) = -46$.

^c From $h_f^0(\text{EtSiMe}_3)$ and $\Delta h_f^0(n-C_4H_{10}/n-C_3H_8) = -22$.

^d From $h_f^{0}(\text{EtCHCl}_2)$ and $\Delta h_f^{0}(\text{CH}_3\text{CH}_2\text{CH}_3/\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3) = -22$.

^e From $h_f^0(H_2C(C_6H_5)_2)$ and $\Delta h_f^0(MeC_6H_5/n-C_3H_7C_6H_5) = -42$.

^fEstimated from increments.

^g Ref. [21].

^h From BDE(H, OEt) and Δ BDE(HOCHMe-H/HOCMe₂-H) = -9 [22].

ⁱ Interpolated from refs. [18,20].

 j From BDE(C₆H₅OCOCH₂-H) [24] and Δ BDE(RCHMe-H/RCH₂-H) = -15, Δ BDE(RCMeAlk-H/RCHMe-H) = -8ⁱ.

^k From BDE(Me₃SiCH₂-H) [24] and the increment^j.

¹From BDE(H, Cl) and Δ BDE(CH₂Cl-H/MeCHCl-H) = -5 [23].

- ^m From BDE(MeCHCl-H) [23].
- ⁿ From BDE(MeCHC₆H₅-H) and BDE(Me₂CC₆H₅-H) [27].
- ^o From BDE(Cl₂HCCCl₂-H) [24].
- ^p From BDE(MeC(C₆H₅)₂-H) [24].
- ^q From BDE(EtO₂CCH₂-H) [25] and the increment^j.
- ^r From BDE(MeCHCN-H) and BDE(Me₂CCN-H) [26].
- ⁸ From BDE(MeCOCH₂-H) [25] and the increment^j.

Figure 5 shows a plot of the activation energies vs. the estimated reaction enthalpies for $\dot{C}H_2OH$ -addition. In general, the activation energies decrease with increasing exothermicity but the correlation

(11)
$$E_a = 50.92 + 0.26 \cdot H_r$$
 (R² = 0.377)

is poor. Radom et al. [6(c)] found

(12)
$$E_a = 82.60 + 0.56 \cdot H_r$$
 (R² = 0.950)

for the six alkenes $CH_2 = CHX$ (X = H, NH₂, F, Cl, CHO, CN), i.e., a much better correlation. Our data for X = H, Cl, CN agree with their result but the other substituents cause large and scattered deviations.

Polar substituents effects can be discussed in terms of the state correlation model [2(c),6,28] which considers the transition state as a combination of four principal valence-bond configurations of the parent reaction system $\dot{R} + A$, namely $\dot{R}A$, \dot{R}^3A , $R^+\dot{A}^-$, and $R^-\dot{A}^+$. Here $\dot{R}A$ represents the educt ground state, for \dot{R}^3A the alkene is in its lowest excited triplet, and $R^+\dot{A}^-$ and R^-A^+ are the lowest charge-transfer states. In the absence of polar effects the transition state is a combination of $\dot{R}A$ and configuration \dot{R}^3A which lies about 250–350 kJ/mol above the ground state of the educts. The energies of the charge-transfer states are estimated with respect to $\dot{R}A$ by $IP(\dot{R}) - EA(A)$ and $IP(A) - EA(\dot{R})$, i.e., from ionization energies and electron affinities. For $\dot{C}H_2OH$ one has $IP(\dot{R}) = 7.56 \text{ eV}$ [5] and $EA(\dot{R}) = -0.14 \text{ eV}$ [6(c)], and the corresponding quantities for the alkenes are also listed in Table III. For our alkenes $R^+\dot{A}^-$ lies 7.5–10 eV, and $R^-\dot{A}^+$ lies 8.1–11.1 eV above $\dot{R}A$. These energies are high but they are lowered in the transition state via Coulomb attraction by an estimated 6.5 eV [2(c)]. A comparison with the energy of \dot{R}^3A then suggests that the configuration $R^+\dot{A}^-$ may contribute to the transition state for most of the alkenes,



Figure 5. Activation energies for the addition of $\dot{C}H_2OH$ to alkenes vs. estimated reaction enthalpies.

especially those with EA ≥ -1.5 eV, whereas $R^-\dot{A}^+$ should play a role only for a few with IP ≤ 8.5 eV, i.e., the ethers and the styrenes.

Figure 6 shows a plot of the activation energies vs. the alkene electron affinities and represents the correlation

(13)
$$E_a/kJ/mol = 15.86 - 7.38 \cdot EA/eV$$
 (R² = 0.773).

For the rate constants a similar good correlation

(14)
$$\log k_{298}/M^{-1}s^{-1} = 5.57 + 1.53 \cdot EA/eV$$
 (R² = 0.820)

was obtained. The theoretical results [6(c)] lead to

(15)
$$E_a/kJ/mol = 14.23 - 10.09 \cdot EA/eV$$
 (R² = 0.839)

which is compatible with eq. (13). No correlation was found between E_a and IP.

Figures 5 and 6 do not provide a clear separation between enthalpy and polar effects but indicate a dominance of the latter in the sense of partial electron transfer from $\dot{C}H_2OH$ to the alkene at least for the alkenes with strong electron withdrawing groups such as 2 Cl, CO₂R, CHO, and CN. These react faster than styrene although their reactions are less exothermic. The separation is also hindered by a correlation between H_r and EA which is obvious from Table III: Alkenes with high electron affinities also give rise to large reaction exothermicities, and this may preserve a linearity in the activation energy vs. enthalpy plot even if there is no direct enthalpy effect [2(c),6(c)].

To our opinion the following findings further support a nucleophilic charge transfer dominated addition behavior: (a) In Figures 5 and 6 the styrene activation energies are above the average correlation. While this is against strong enthalpy effects it also disfavors charge-transfer contributions of the type $R^-\dot{A}^+$ which were considered



Figure 6. Activation energies for the addition of CH_2OH to alkenes vs. alkene electron affinities.

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to be likely above. On the other hand, this deviation is early understood in terms of a frontier molecular orbital description of the transition state [29]. A nucleophilic behavior means a dominant stabilization of the transition state by SOMO-LUMO interactions, and for the styrenes these are diminished by the low LUMO coefficient at the attacked carbon; (b) Correlations like eq. (14) were obtained previously [2] for the radicals tert-butyl, $\log k/M^{-1}s^{-1} = 6.24 + 1.66 \cdot EA(eV)$, and 2-hydroxy-2-propyl, log $k/M^{-1}s^{-1} = 6.64 + 1.71 \cdot EA(eV)$. In comparison, the slopes of the correlations reflect the order of the ionization potentials of the radicals, namely 1.53 vs. IP = 7.56 eV for CH_2OH , 1.66 vs. 6.7 eV for $C(CH_3)_3$ and 1.71 vs. 6.49 eV for $(CH_3)_2COH$. For the whole series of alkenes hydroxymethyl is the least selective and the least reactive of the three nucleophilic radicals; (c) As in refs. [2(b),(c)] an analysis was performed with the ratios of rate constants derived from the data of Table II. In the vast majority of cases we found the larger rate constant for the alkene with the larger electron affinity irrespective of the reaction enthalpy difference, and there were only a few cases for which the reactivity ratio could be dominated by the reaction enthalpy. However, this analysis gave a less clear picture than for the more nucleophilic 2-hydroxy-2-propyl radical for which no case for an enthalpy dominance was discovered [2(b)]. To illustrate this point more clearly we consider the ratio of rate constants of α -methylvinylacetate and vinylacetate which should be larger than one if enthalpy effects and smaller than one if nucleophilic charge-transfer effects dominate. The experimental ratios are 1.93 for $(CH_3)_2CCN$ which also showed an overall enthalpy controlled behavior and 0.65 for the extremely nucleophilic $(CH_3)_2COH$ [2(b),(c)]. For hydroxymethyl Table II gives 1.15 which indicates a noticable effect of the enthalpy within the gross picture of a nucleophilic character; and (d) Steenken et al. [4] have reported rate constants for the addition of CH_2OH to p-substituted nitrobenzenes in aqueous solution at 20°. There, the addition occurs at the N =O double bond but it is interesting to observe that our correlation (14) reproduces the rate constants quite well, i.e., the two reactions exhibit a similar degree of charge-transfer.

In conclusion, the rate constants for the sterically unhindered addition of CH_2OH are highly governed by charge transfer effects which reflect the nucleophilicity of this radical. Effects of the overall reaction enthalpy may contribute but are not clearly expressed. The experimental results confirm the high predictive power of high level ab initio calculations on radical addition barriers and enthalpies [6(c)]. Moreover, they confirm that contributions of the charge-transfer state $R^+\dot{A}^-$ become important if this state is less than about 9 eV above the reactant ground state [6(c)], but for contributions of $R^-\dot{A}^+$ a lower energy seems necessary.

Note added in proof: A referee has analyzed our rate constants in terms of the Hammett relation $\log k = \rho \cdot \sigma + C$ using σ_p values and found good correlations for two separate sets: (1) X and Y are nonmesomeric substitutents and (2) X and Y are mesomeric. The positive slopes confirm the nucleophilicity of CH_2OH addition, and the separation in two sets reflects the fact that for substituents like Ph, CN, and COOR the rates are increased by enthalpy effects due to the resonance stabilization of the adduct radicals. While this analysis is worthwhile we wish to point out that alkene electron affinities correlate well with Hammett sigmas [2]. Hence, the choice of the basis for rate constant correlations is a matter of taste. The same applies to the suggestion of a second referee to use redox potentials instead of ionization potentials and electron affinities because they refer to solutions.

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