Absolute Rate Constants and Arrhenius Parameters for the Addition of the Methyl Radical to Unsaturated Compounds: The Methyl Affinities Revisited

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Received September 5, 1997[⊗]

Abstract: Absolute rate constants and their Arrhenius parameters are reported for the addition of the methyl radical to 21 monosubstituted and 1,1-disubstituted alkenes and to 6 benzenes in 1,1,2-trifluoro-1,2,2-trichloroethane solution. They are used to convert relative reaction rates known as methyl affinities from the work of M. Szwarc and others for about 250 additional unsaturated compounds to the absolute scale. An analysis shows that the addition rates depend on the reaction enthalpy but also indicates a moderate nucleophilic polar effect for the liquid-phase reactions. It is pointed out that this polar effect may be smaller in the gas phase.

Introduction

About four decades ago, M. Szwarc and co-workers[1] measured an impressive set of about 200 relative rate constants for the addition of the methyl radical to various unsaturated organic compounds. These are ratios of the addition rate constant to the rate constant for hydrogen abstraction from 2,2,4-trimethylpentane (isooctane), and were determined mostly at 50−85 °C. From the so-called methyl affinities Szwarc deduced a variety of factors which influence the reaction barrier, such as the exothermicity of the reaction, the energy location of the first excited triplet state of the reactants, and the steric blocking by bulky substituents at the attacked carbon atom. He even correctly concluded the now accepted structure of the transition state. Polar substituent effects were found to be small and in the direction of a slight radical nucleophilicity. The methods were simple and allowed the detection of abstraction besides addition reactions. Hence, they were also applied by others to obtain additional methyl affinities[2,3] and extended to additions

of the ethyl,[4] the *n*-propyl,[5] the cyclopropyl,[6] and the trifluoromethyl[1a,d,7−11] radicals.

Though some reviews are available[12−14] Szwarc's results have only been quoted occasionally in the more recent literature, and some criticism of the methodology has arisen.[15] However, in previous work we found an excellent correlation of the methyl affinities with absolute rate constants for the addition of methyl to 20 alkenes at room temperature as obtained by time-resolved ESR spectroscopy.[16] This reassured the quality of the earlier relative data.

Continuing our work on absolute rate constants for the addition of carbon centered radicals to unsaturated compounds and the factors controlling them[16,17] we now present additional rate data and Arrhenius parameters for the reaction of methyl with alkenes and other unsaturated compounds. These allow us to convert the methyl affinities to absolute rate constants and their Arrhenius parameters, and lead to an unparalleled large set of absolute addition rate data now available for further analysis and discussion. On the basis of the new experimental

[⊗] Abstract published in *Advance ACS Abstracts,* December 15, 1997.

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data and the converted methyl affinities we further discuss the factors governing the barriers for the addition of methyl with special emphasis on alkenes and on the role of the polar effect which has recently severely been questioned.[18]
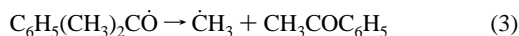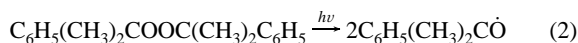
Experimental Procedures and Analysis

The general experimental arrangement and the procedures for kinetic ESR spectroscopy have been described previously.[16,17] In principle, deoxygenated solutions of a photochemical radical precursor in an inert solvent flow slowly through a thermostated flat cell in the ESR cavity and are irradiated by UV light. During continuous photolysis and in the absence of reactive substrates one observes the radical whose kinetics is to be studied. In the presence of reactants its ESR spectrum is replaced by those of secondary radicals, and their structures reveal the type of reaction. Intermission of the photolysis by a rotating sector and coherent sampling of the time-dependent signal of the primary radical leads to kinetic traces which are then analyzed according to the appropriate rate laws. In the absence of substrate and in inert solvents one observes a pure second-order radical self-termination, possibly slightly disturbed by a pseudo-first-order reaction with the solvent, the precursor, or impurities. In the presence of reactants the pseudo-first-order contribution increases due to the reaction to be examined. In the off-period of photolysis the radical decay profile obeys the following:

$$R(t) = R(0) \exp(-t/\tau_1)/(1 + t/\tau_2) \tag{1}$$

The pseudo-first-order rate $\tau_1^{-1} = \tau_{10}^{-1} + k[S]$ reflects the side reaction (τ_{10}) and the reaction with the substrate (k), and the second-order lifetime $\tau_2^{-1} = 2k_tR(0)$ is due to the termination reactions. Equation 1 is exact if all concurring termination reactions have the same rate constants and/or if the pseudo-first-order processes contribute little to the overall decay. Though the first condition is approximately fulfilled for all small alkyl radicals, the latter ($\tau_1 \gg \tau_2$) was also obeyed here by using low enough substrate concentrations.

In the course of this work the experimental arrangement was improved considerably by installation of an ESR spectrometer with a higher time resolution (Bruker EMX, 10 μs minimum response time), by increasing the stability of the sector frequency to 0.05% and by using a new home-built PC-based control, data aquisition, and analysis system with a common precise clock.

Methyl radicals were produced by photolysis of dicumyl peroxide, *i.e.*, the reactions[19]

$$C_6H_5(CH_3)_2COOC(CH_3)_2C_6H_5 \xrightarrow{h\nu} 2C_6H_5(CH_3)_2C\dot{O} \tag{2}$$

$$C_6H_5(CH_3)_2C\dot{O} \rightarrow \dot{C}H_3 + CH_3COC_6H_5 \tag{3}$$

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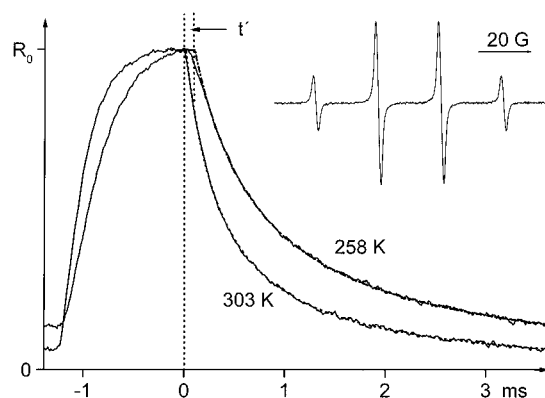
Figure 1. ESR spectrum of the methyl radical (inset) and kinetic traces in 1,1,2-trifluoro-1,2,2-trichloroethane.

Since both the cumyloxy and the methyl radical are highly reactive, various precautions had to be taken to avoid side reactions. Thus, the peroxide (Aldrich) was recrystallized at least 4 times from methanol, and 1,1,2-trichloro-1,2,2-trifluoroethane of the highest available purity (SDS, Peypin, >99.5%) was chosen as a fairly inert solvent. It was found that the product acetophenone photosensitizes the peroxide decomposition,[19b] and, hence, it was added deliberately. Optimum concentrations were 0.022 M peroxide and 0.020 M acetophenone.

GLC analysis of the photolyzate in the absence of further substrates yielded ethane and acetophenone as major products (>90%), as well as methane, methyl chloride, benzene, chlorobenzene, toluene, possibly acetone, and further unidentified compounds in minor amounts (total <10%). Obviously, reactions 2 and 3 are dominant, and the minor products point to reactions of methyl with the solvent, the peroxide, and acetophenone, and to a minor cleavage pathway of cumyloxy leading to acetone and phenyl radicals.[20]

Figure 1 shows the familiar ESR spectrum of the methyl radical (inset, 297 K, $g = 2.0025$, $a_H = -22.83$ G) and its concentration vs time profiles in the absence of substrates at 303 and 258 K. For $T > 273$ K the decay is well described by eq 1, but for lower temperatures there are deviations because then reaction 3 is noninstantaneous on the experimental time scale. Simulations of decay profiles showed that this delayed formation of methyl can simply be taken into account by a shift of zero time t' in eq 1

$$R(t) = R(0) \exp(-(t - t')/\tau_1)/(1 + (t - t')/\tau_2) \tag{4}$$

where $t' = k_3^{-1}$, i.e., the rate of the first-order cumyloxy fragmentation of reaction 3. Equation 4 was found generally useful for the study of radical rearrangements and other reactions as will be discussed elsewhere, and fits to this formula are superimposed on the experimental data in Figure 1. Analyses at various temperatures lead to the Arrhenius parameters for the fragmentation of the cumyloxy radical (E_a given in kJ/mol and errors in units of the last quoted digit)

$$\log(k_3/s^{-1}) = 13.3(3) - 45.2(10)/2.303RT \tag{5}$$

the self-termination of methyl in 1,1,2-trichloro-1,2,2-trifluoroethane

$$\log(2k_t/M^{-1} s^{-1}) = 12.8(1) - 14.7(4)/2.303RT \tag{6}$$

and the rate of the pseudo-first-order side reaction

$$\log(\tau_{10}^{-1}/s^{-1}) = 4.2(3) - 12.4(11)/2.303RT \tag{7}$$

At 303 K the rate constant for the fragmentation in reaction 3 is $k_3 = 300\,000$ s^{-1}, and agrees very well with $k_3 = 340\,000$ s^{-1} reported by Avila et al.[19a] for CCl$_4$ solvent. Also, the Arrhenius parameters are close to $\log(k_3/s^{-1}) = 12.4(6) - 36.0(19)/2.303RT$ for chlorobenzene solvent.[21] The self-termination of methyl is at the diffusion controlled limit ($2k_t(298) = 1.7 \times 10^{10}$ M^{-1} s^{-1}), and eq 7 was used later on to

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Table 1. Absolute Rate Constants and Arrhenius Parameters for the Addition of Methyl Radicals to Unsaturated Compounds

substrate	n^a	T, K	log A, $M^{-1} s^{-1}$	E_a, kJ/mol	k_{297}, /$M^{-1} s^{-1}$
propene	12	297			4300
ethene	16	297			7000^c
1-butene	14	297			7600
2-methylpropene	11	297			8500
2-methoxypropene	19	297			12000
isopropenyl acetate	30	297			12000
vinyl acetate	68	273−313	8.4 (+2/−4)^b	23.9 (15)	14000
ethyl vinyl ether	26	297			14000
vinyl chloride	12	297			20000
trimethylvinylsilane	160	273−313	8.1 (+1/−2)	20.8 (7)	23000
isopropenyl chloride	31	297			35000
styrene	39	273−313	8.9 (+2/−3)	19.9 (11)	260000
α-methylstyrene	90	263−313	8.8 (+1/−2)	18.9 (8)	310000
1,1-dichloroethene	78	253−313	8.9 (+2/−3)	19.1 (13)	320000
methyl acrylate	33	297			340000
methyl methacrylate	86	273−313	8.9 (+1/−2)	18.2 (10)	490000
acrylonitrile	17	297			610000
acrolein	16	297			740000
isoprene	70	273−313	8.6 (+2/−4)	17.1 (15)	760000
methacrylonitrile	106	283−313	8.9 (+2/−4)	16.9 (14)	760000
1,1-diphenylethene	35	263−313	7.9 (+1/−2)	11.3 (8)	780000
benzene	39	283−333	8.2 (+1/−2)	37.2 (8)	46
fluorobenzene	50	273−313	8.9 (3)	40.9 (22)	54
chlorobenzene	34	296−313	10.2 (4)	45.3 (47)	170
benzonitrile	5	296−313	10.3 (7)	43.2 (113)	500
1,4-dichlorobenzene	7	296−313	9.7 (5)	42.8 (55)	860
1,3,5-trichlorobenzene	6	296−313	9.9 (5)	35.8 (42)	4000

^{a} Number of kinetic runs. ^{b} Errors in units of the last digit given. ^{c} 3500 $M^{-1} s^{-1}$ per CH_2 group.
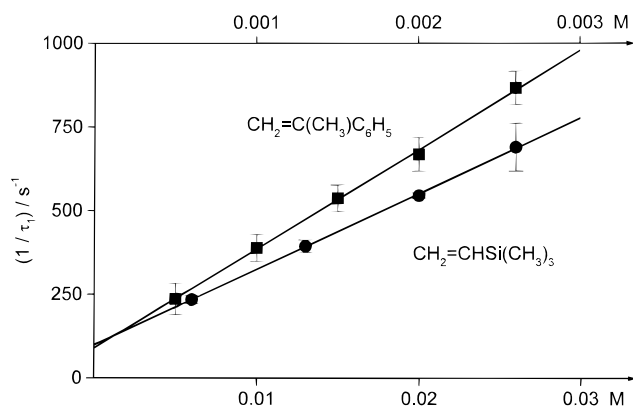
Figure 2. Pseudo-first-order plots for the reaction of the methyl radical with α-methylstyrene and trimethylvinylsilane.

Figure 3. Temperature dependence of the addition rate constant of the methyl radical to α-methylstyrene and 1,1-diphenylethene and fits to the Arrhenius equation. The squared symbols are data derived from methyl affinities.
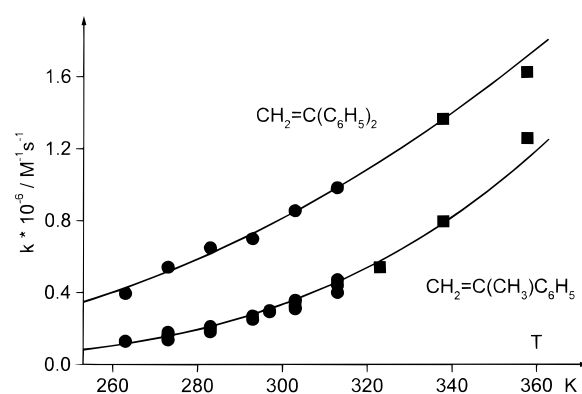
supply the correction factor t_{10} in the analyses of the reactions of methyl with unsaturated substrates.

For several alkene substrates used in relatively high concentrations ESR spectra of the secondary radicals were taken during continuous photolysis. As expected, they are adducts to the unsubstituted alkene carbon atom. Their ESR data are given in the Supporting Information, and agree with earlier literature.[22]

Figure 2 displays pseudo-first-order plots for the reactions of methyl with α-methylstyrene and trimethylvinylsilane. The intercept of the ordinate reflects the side reactions, and the rate constants for the reaction with the alkenes follow from the slopes of the straight lines. Measurements at various temperatures in the range 263 K < T < 313 K gave the Arrhenius parameters of the reaction rate constants, and two fits of the Arrhenius equation to the data are shown in Figure 3.

Results

Table 1 gives absolute rate constants at room temperature and Arrhenius parameters for the reaction of the methyl radical with 20 mono- and 1,1-disubstituted alkenes, one diene, and 6 substituted benzenes. All reactions are believed to be by

addition only, as established earlier in Szwarc's work[1] and in part confirmed here by the direct observation of the adduct radicals. The statistical errors of the rate constants are below 20%. However, for ethyl vinyl ether and 2-methoxypropene hydrogen abstraction may compete,[1] and the rate constants are therefore tentative. Small deviations from our previous data[16] are due to the now increased number of experiments.

To convert Szwarc's methyl affinities to absolute values the Arrhenius parameters for the hydrogen abstraction reaction from 2,2,4-trimethylpentane are required. Unfortunately, the kinetics of this reaction could be directly studied only with low precision and at room temperature, since the rate constant is rather low, and since secondary reactions of the cumyloxy radical and of excited acetophenone with the alkane strongly interfered. The result is $k_{TMP}(297) = (190 + 50/−100)$ $M^{-1} s^{-1}$. More reliable rate constants were obtained indirectly in the following way: Szwarc et al. measured the Arrhenius parameters for the methyl affinities of ethene, propene, 2-methylpropene, styrene, α-methylstyrene, and isoprene (for references, see Table 2). Combination with our addition rate constants measured at 297 K

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Table 2.   Representative Methyl Affinities Converted to Absolute Rate Constants and Arrhenius Parameters

compound	k/k_{TMP} (338 K)	k_{338}, M^{-1} s^{-1}	log A, M^{-1} s^{-1}	E_a, kJ/mol	ref
		Alkenes and Isolated Double Bonds			
ethene	38.4	3.3×10^4	9.3[a]	31.4	1l,j,m,y,ad
propene	22.0[b]	1.9×10^4	9.3[a]	32.3	1l,p,x,y,ad
1-butene	27[b]	2.3×10^4	7.8[a]	22.5	1l,m,p,x
1-pentene	25[b]	2.1×10^4			1l,p
1-heptene	26[b]	2.2×10^4			1l,p
1-decene	22[b]	1.9×10^4			1l,p
ethyl vinyl ether	8	6900			1r
vinyl acetate	34	2.9×10^4	7.4[a]	18.9	1b,f,r
methyl acrylate	1030	8.8×10^5			1ac
methyl vinyl ketone	1900	1.6×10^6			1ac
acrylonitrile	1730	1.5×10^6	9.0[a]	18.1	1f,ac
styrene	790	6.8×10^5	9.2[a]	21.6	1b,f,r,p,y
2,4,6-trimethylstyrene	104[b]	8.9×10^4			1u
2-chlorostyrene	1000	8.6×10^5			1u
3-chlorostyrene	1040	8.9×10^5			1u
4-chlorostyrene	1020	8.8×10^5			1u
2,5-dichlorostyrene	1210	1.0×10^6			1u
1-vinylnaphthalene	810	7.0×10^5			1u
1-vinylanthracene	1350	1.2×10^6			1u
9-vinylanthracene	440	3.8×10^5			1u
vinyl bromide	292[d]	2.5×10^5			2
vinyl chloride	219[d]	1.9×10^5			2
vinyl fluoride	20.3[d]	1.7×10^4			2,3a
2-methylpropene	36[b]	3.1×10^4	8.9[a]	28.1	1l,m,p,y
α-methylstyrene	930	8.0×10^5	8.8[a]	18.7	1r,y
methyl methacrylate	1450	1.2×10^6	8.6[a]	16.3	1f,r,1ac
methacrylonitrile	2120	1.8×10^6			1ac
1,1-dichloroethene	1020[d]	8.8×10^5			2
1,1-difluoroethene	24.9[d]	2.1×10^4			2,3a
1,1-diphenylethene	1600	1.4×10^6	7.7[a]	10.5	1b,f,k
cyclopentene	5.8	5000			1aa
cyclohexene	0.9	770			1aa
cycloheptene	4.2	3600			1aa
cyclooctene	6.7	5800			1aa
(E)-2-butene	6.9[b]	5900	7.7	25.3	1d,i,l,m,p
(Z)-2-butene	3.4[b]	2900	7.4	25.2	1d,i,l,m,p
(E)-β-methylstyrene	90[b]	7.7×10^4			1p,u
(Z)-β-methylstyrene	40[b]	3.4×10^4			1u
(E)-stilbene	105	9.0×10^4	8.3	21.4	1b,e,f,k
(Z)-stilbene	29.0	2.5×10^4	8.2	24.2	1k
diethyl fumarate	2000	1.7×10^6	6.9	4.1	1k,r
fumarodinitrile	1930	1.7×10^6	8.5	14.2	1k,r
diethyl maleate	333	2.9×10^5	7.7	14.4	1b,f,k,r
maleodinitrile	1930	1.7×10^6	9.9	23.6	1k,r
2-methyl-2-butene	5.6	4800			1p
α,β-dimethylstyrene	66	5.7×10^4			1u
β,β-dimethylstyrene	15.4	1.3×10^4			1t
β,β-dimethyl methylacrylate	12	1.0×10^4			1ac
β,β-dimethylacrylonitrile	23.5	2.0×10^4			1ac
triphenylethene	46	4.0×10^4	7.4	18.1	1b,f
trifluoroethene	57.5[d]	4.9×10^4			2,3a
α,β,β-trimethylstyrene	20[b]	1.7×10^4			1u
tetraphenylethene	<10	<8600			1b
tetrachloroethene	<0.3	<2600			1j
tetrafluoroethene	387[d]	3.3×10^5	8.8	21.2	1j,2,3a
hexafluoropropene	60	5.2×10^4			3d
perfluoro-1-octene	39	3.4×10^4			3b,e
1,5-hexadiene	68[b]	5.8×10^4			1p
1,4-cyclohexadiene	<20	$<1.7 \times 10^4$			1s,aa
		Conjugated Multiple Bonds			
1,3-butadiene	2015	1.7×10^6	9.6	21.8	1p,r,y,ad
isoprene	2090	1.8×10^6	9.0[a]	17.6	1r,p,y
chloroprene	7540	6.5×10^6			1p
2,3-dimethyl-1,3-butadiene	2230	1.9×10^6			1r,p
(E)-1,3-pentadiene	840	7.2×10^5			1p
(Z)-1,3-pentadiene	1200	1.1×10^6			1p
4-methyl-1,3-pentadiene	1000	8.6×10^5			1p
1,2-dimethylenecyclobutane	4750	4.1×10^6			1z
1,2-dimethylenecyclohexane	1015	8.7×10^5			1z
1-methoxy-1,3-butadiene	500	4.3×10^5			1p
1-phenyl-1,3-butadiene	2290	2.0×10^6			1p
2,4-hexadiene	180	1.5×10^5	8.3	20.2	1p
cyclopentadiene	270	2.3×10^5			1aa
1,3-cyclohexadiene	665	5.7×10^5			1aa
cycloheptatriene	156	1.3×10^5			1aa
cyclooctatetraene	81	7.0×10^4			1aa

Addition of Me Radical to Unsaturated Compounds

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Table 2 (Continued)

compound	k/k_{TMP} (338 K)	k_{338}, M^{-1} s^{-1}	log A, M^{-1} s^{-1}	E_a, kJ/mol	ref
		Alkynes			
ethyne	29.4	2.5×10^4	9.7	34.3	1n
propyne	10.9	9300	8.8	31.1	1n
1-pentyne	14[b]	1.2×10^4			1n
1-hexyne	17.5[b]	1.5×10^4			1n
phenylethyne	195	1.7×10^5	9.2	25.9	1n
2-butyne	1.4	1200			1n
diphenylethyne	12.0	1.0×10^4	10.5	42.1	1n
		Cumulated Multiple Bonds			
allene	17.6	1.5×10^4	7.6	22.2	1p
1,2-butadiene	14.8	1.3×10^4	8.3	26.8	1p
1,2-pentadiene	19[b]	1.7×10^4			1p
2,3-pentadiene	14[b]	1.2×10^4			1p
tetraphenylallene	52[e]	4.5×10^4			1p
vinylacetylene	2260	1.9×10^6			1ac
		Benzenes			
benzene	0.29	250	9.5[a]	46.0	1a,e,f
toluene	0.48[b]	410			1i
anisol	0.19[c]	163			1o
ethyl benzoate	1.5[c]	1300			1o
acetophenone	0.70[c]	600			1o
benzonitrile	3.6[c]	3000	9.2[a]	36.9	1o
bromobenzene	1.05[c]	900			1o
chlorobenzene	1.23[c]	1050	8.8[a]	37.1	1o
fluorobenzene	0.64[c]	550	10.1[a]	47.3	1o
1,3-dichlorobenzene	3.6[c]	3100			1o
1,4-dichlorobenzene	3.4[c]	2900	7.5[a]	25.8	1o
		Condensed Aromatic Compounds			
naphthalene	9.4	8100	8.2	27.7	1a,e,v
1-methylnaphthalene	8.1	7000			1v
2-methylnaphthalene	13.0	1.1×10^4			1v
1-methoxynaphthalene	8.8	7600			1v
2-methoxynaphthalene	7.5	6400			1v
1-methyl naphthoate	19.4	1.7×10^4			1v
2-methyl naphthoate	40.3	3.5×10^4			1v
1-acetonaphthone	20	1.7×10^4			1v
2-acetonaphthone	44	3.8×10^4			1v
1-naphthonitrile	31	2.6×10^4			1v
2-naphthonitrile	46	3.9×10^4			1v
1-bromonaphthalene	8	7000			1v
2-bromonaphthalene	21.2	1.8×10^4			1v
1-chloronaphthalene	13.2	1.1×10^4			1v
2-chloronaphthalene	21.6	1.9×10^4			1v
1-fluoronaphthalene	10.5	9000			1v
2-fluoronaphthalene	13.2	1.1×10^4			1v
1,4-dichloronaphthalene	20.6	1.8×10^4			1v
acenaphthene	4.7	4000			1v
anthracene	385	3.3×10^5	9.4	25.0	1a,e,t,w
1-methylanthracene	355	3.1×10^5			1t
2-methylanthracene	355	3.1×10^5			1t
9-methylanthracene	190	1.6×10^5			1t
phenanthrene	10.2	8800	9.3	34.8	1a,e,g,t
2-methylphenanthrene	13	1.1×10^4			1t
3-methylphenanthrene	12	1.1×10^4			1t
9,10-dimethylphenanthrene	6.0	5200			1t
naphthacene (358 K)	3700	6.2×10^6			1f
benzo[a]anthracene (358 K)	206[e]	3.4×10^5			1h
benzo[c]phenanthrene (358 K)	25.5[e]	4.2×10^4			1c
pyrene (358 K)	49	8.1×10^4			1a,e
chrysene (358 K)	23	3.8×10^4			1f
benzo[a]pyrene (358 K)	268[e]	4.5×10^5			1h
dibenz[a,h]anthracene (358K)[e]	148	2.5×10^5			1h
hexahelicene (358 K)	114[e]	1.9×10^5			1h
		Quinones			
1,4-benzoquinone	6050[e]	5.2×10^6			1d,f
2-methylbenzoquinone	4150	3.6×10^6			1d,f
2-methoxybenzoquinone	3180	2.7×10^6			1f
2-chlorobenzoquinone	1×10^4	8.9×10^6			1d,f
2,3-dimethylbenzoquinone	3090[e]	2.7×10^6			1q
2,6-dimethoxybenzoquinone	1020[e]	8.8×10^5			1q
2,3-dichlorobenzoquinone	4000[e]	3.4×10^6			1q
2,6-dichlorobenzoquinone	1.6×10^4 [e]	1.3×10^7			1f
duroquinone	39	3.4×10^4			1d,f
chloranil	120	1.0×10^5			1d,f
1,2-naphthoquinone	1370	1.2×10^6			1d,f

Table 2 (Continued)

compound	k/k_{TMP} (338 K)	k_{338}, M^{-1} s^{-1}	log A, M^{-1} s^{-1}	E_a, kJ/mol	ref
		Quinones			
1,4-naphthoquinone	3240	2.8×10^6			1q
2-methyl-1,4-phthoquinone	1350	1.2×10^6			1d,f
2-chloro-1,4-naphthoquinone	6500^e	5.6×10^6			1q
2-*tert*-butylanthraquinone	36	3.1×10^4			1d,f
phenanthraquinone	280	2.4×10^5			1d,f
		Heterocycles			
pyridine (358 K)	1.2	2000	7.0	25.6	1a,e
acridine	187	1.6×10^5	9.8	29.4	1e,f,w
quinoline	13	1.2×10^4	7.9	24.7	1a,e,w
isoquinoline (358 K)	14	2.3×10^4			1e,f,w
phenazine	107	9.2×10^4			1w

^{a} From converted methyl affinities and rate constants measured in this work. ^{b} Abstraction also observed. ^{c} Original data relative to the reactivity of benzene, converted via $k_{Ben}/k_{TMP} = 251/858$ at 65 °C. ^{d} Original data relative to the reactivity of ethene, converted via $k_{Eth}/k_{TMP} = 38.4$ at 65 °C.[1ad] ^{e} Original data relative to the reactivity of toluene, converted via $k_{Tol}/k_{TMP} = 3$.[1i]
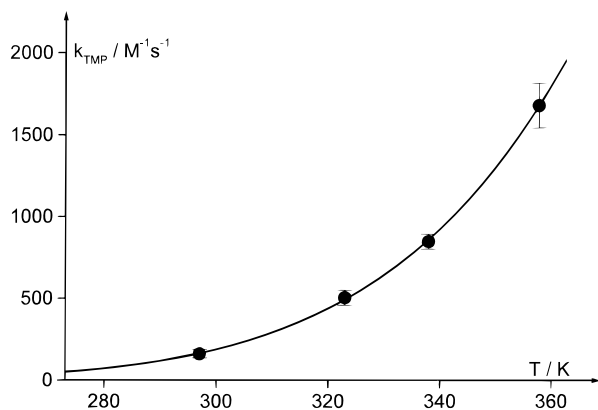
Figure 4. Temperature dependence of the reaction rate constant of methyl with 2,2,4-trimethylpentane and fit to the Arrhenius equation.

(Table 1) gives $k_{TMP}(297) = (162 \pm 25)$ M^{-1} s^{-1}. For 323, 338, and 358 K, Szwarc's methyl affinities for the addition to styrene, α-methylstyrene, and isoprene and the Arrhenius parameters from this work were used for the conversion. The same procedure was applied for 338 and 358 K for 1,1-diphenylethene and methyl methacrylate, and finally for 338 K for 1,1-dichloroethene and methacrylonitrile. The resulting temperature dependence of k_{TMP} is shown in Figure 4 and is given by

$$\log(k_{TMP}/\text{M}^{-1}\,\text{s}^{-1}) = 8.13(7) - 33.6(5)/2.303RT \quad (8)$$

with E_a in kJ/mol.

Moreover, the Arrhenius parameters of k/k_{TMP} for styrene, α-methylstyrene, and isoprene are known.[1b,f,r,p,y] Combination with our data of Table 1 yields

$$\log(k_{TMP}/\text{M}^{-1}\,\text{s}^{-1}) = 8.0(2) - 32.5(12)/2.303RT \quad (9)$$

By using all available conversions and proper error weighting the average becomes

$$\log(k_{TMP}/\text{M}^{-1}\,\text{s}^{-1}) = 8.08(30) - 33.30(200)/2.303RT \quad (10)$$

and this relation was used to obtain the final absolute data from the methyl affinities. To check the procedure we included the rate constants derived from methyl affinities at higher temperatures in the plots of the temperature dependence observed here. As demonstrated in Figure 3, they agree very well with the Arrhenius parameters derived from our experimental data which are measured at lower temperatures.

Table 2 gives a representative selection of methyl affinities converted to absolute rate constants and their temperature dependence. Our new experimental data at room temperature were included in the redetermination of the Arrhenius parameters which, therefore, differ slightly from those given in Table 1. Data for 95 additional compounds are available as Supporting Information.

For comparison only a few absolute rate constants for the addition of methyl radicals in liquid solutions are available. By pulse radiolysis and for aqueous solution Thomas[23] reported $k(297) = 4.9 \times 10^3$, 5.3×10^3, 3.0×10^4, 3.9×10^4, and 1.2×10^6 M^{-1} s^{-1} for ethene, propene, 1-butene, 2-methylpropene and 1,3-butadiene, respectively. Most of these data are slightly higher than ours and the converted methyl affinities (Tables 1 and 2), but the overall agreement is fair. The same holds for Gilbert's[24] $k(297) = 5.0 \times 10^5$, 5.8×10^6, and 1.0×10^5 M^{-1} s^{-1} for methacrylic acid, methyl methacrylic acid, and crotonic acid in water, which are slightly higher but similar to our values for the esters, and for $k(297) = 1.2 \times 10^6$ M^{-1} s^{-1} for benzoquinone,[25] again in aqueous medium. Since there are no gross differences between the rate constants in the low polar 1,1,2-trichloro-1,2,2-trifluoroethane ($\epsilon = 2.42(2)$) and in aqueous solution, the addition behavior of the methyl radical is not strongly solvent dependent, though the rate constants seem to increase slightly with increasing solvent polarity. This also ensures the validity of the conversion procedure for the methyl affinities which were measured in the unpolar solvent 2,2,4-trimethylpentane[1] and converted with rate data obtained here in 1,1,2-trifluoro-2,1,1-trichloroethane.

A comparison of the solution with gas-phase data (see Supporting Information) shows that for all compounds except benzene the latter are lower by more than 1 order of magnitude. For ethene and ethyne the gas-phase data have been reevaluated several times[26,27] and are believed to be accurate to a factor of 2, so that their differences to the solution rates are particularly noteworthy. Averaging of the frequency factor differences for the individual compounds in the two phases gives $\log(A_l/\text{M}^{-1}\text{s}^{-1}) - \log(A_g/\text{M}^{-1}\text{s}^{-1}) = +0.41 \pm 0.69$, i.e., an insignificant

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value. If benzene is omitted, the average difference of the experimental activation energies is $E_{ag} - E_{al} = (3.0 \pm 4.7)$ kJ/mol, and from the ratio of rate constants one obtains for equal frequency factors in the two phases $E_{ag} - E_{al} = (6.5 \pm 2.8)$ kJ/mol. This difference may be significant and may reflect a true solvation effect on the solution data. It would be in keeping with the slight solvent polarity dependence noticed above. On the other hand, the gas-phase data have all been determined relative to other rate constants and date back many years. Moreover, the most recent work on ethene, ethyne, and benzene[28] gives errors which still allow order of magnitude variations.

Discussion

In the following we will mainly discuss the factors controlling the rates for the addition of methyl to the mono- and 1,1-substituted alkenes. Their frequency factors are in the range $7.4 < \log(A/M^{-1}\ s^{-1}) < 9.2$ (Table 1) and show no specific variation with the substituents. Therefore, we consider the spread insignificant and likely to be caused by error compensation of the Arrhenius parameters. The average of all data is $\log(A/M^{-1}\ s^{-1}) = 8.6 \pm 0.5$. This is very close to the average frequency factors for the addition of other primary radicals to the same alkenes as $\log(A/M^{-1}\ s^{-1}) = 8.7 \pm 0.3$ for cyanomethyl, $\log(A/M^{-1}\ s^{-1}) = 8.4 \pm 0.1$ for *tert*-butoxycarbonylmethyl, $\log(A/M^{-1}\ s^{-1}) = 8.1 \pm 0.1$ for hydroxymethyl, and $\log(A/M^{-1}\ s^{-1}) = 8.6 \pm 1.3$ for benzyl.[17a] From symmetry considerations methyl should have a $\Delta \log(A/M^{-1}\ s^{-1}) = \Delta \log 3 = 0.477$ higher frequency factor than the other species, but this is within the error limits. Hence, the data suggest a common value of $\log(A/M^{-1}\ s^{-1}) = 8.5 \pm 0.5$ for additions of primary alkyl radicals to the CH_2 group of mono- and 1,1-disubstituted alkenes both in solution and in the gas phase. If correct, this suggests a minimum error of the activation energies of about 3 kJ/mol.

The common frequency factor means that for all cases studied the structures of the transition states are very similar, and this agrees with the results of several quantum chemical calculations.[18,29] Hence, the variation of the addition rate constants with the alkene substituents is caused mainly by their influence on the activation energy, as has been stated previously by Tedder.[30] At 297 K, the rate constants vary with substitution from 4 300 to 780 000 $M^{-1}\ s^{-1}$, i.e., by a factor of 200, and the activation energies range from 10.5 to 31.4 kJ/mol (tables). In comparison to several other alkyl radicals[17] these ranges are small. In particular, the methyl radical is much less selective and for some alkenes also less reactive than the hydroxymethyl,[17i] the 2-hydroxy-2-propyl,[17g,n] and the *tert*-butyl radical,[17b] and its reaction behavior resembles that of the cyanomethyl and the *tert*-butoxycarbonylmethyl species,[17j] though the latter radicals are generally more reactive by up to a factor of 10.[17a]

For mono- and 1,1-disubstituted alkenes steric substituent effects on the addition rates should be small. Therefore, the reaction barriers should be governed mainly by enthalpic and/

or polar substituent effects.[17,30,31] If the enthalpy effect dominates, the activation energies decrease and the rate constants increase with increasing reaction exothermicity. This behavior has been found clearly expressed for two cyano- and a carboxy-substituted alkyl radical[17g,j] and for the benzyl and the cumyl species.[17k] Polar effects are due to a partial charge transfer in the transition state. Within the frame of the state correlation diagram for radical additions[32] they reflect contributions of the configurations R^+A^- and R^-A^+ to the wave function where R denotes the radical and A the alkene. These are of particular importance for the transition state geometry since there the energies of the charge transfer states are considerably lowered by the Coulomb attraction. For several radicals with low ionization energies, such as hydroxymethyl, 2-hydroxypropyl, and *tert*-butyl, the contribution of the state R^+A^- was found dominant. The barriers for their additions decreased with increasing electron affinity of the alkene,[17] and there was no clear correlation with the reaction enthalpy. These radicals react with alkenes carrying strongly electron withdrawing substituents even faster than with phenyl-substituted compounds such as styrene for which the exothermicity is higher, and this can be taken as a clear criterion for a polar effect. On the other hand, radicals with high electron affinities, such as perfluoroalkyls and dicyanomethyl, are electrophilic, and their reaction barriers increase with decreasing alkene ionization energy.[33]

Now, the methyl radical has a rather high ionization energy of 9.84 eV and a low electron affinity of 0.08 eV.[34] Hence, the polar effects should not be large. The bond dissociation energy of methane exceeds that of other CH bonds,[35] and makes the addition of methyl more exothermic than that of other alkyl radicals.

For the methyl radical strong effects of the reaction enthalpy have already been pointed out by Szwarc[1] in terms of the adduct radical stabilization, of the radical localization energies, and of strain in the attacked bond, and there are many clear-cut examples in Table 2 (cf. ethene vs 1,3-butadiene, benzene vs naphthalene, etc.). Szwarc also noticed a weak nucleophilicity[1o,r,u,v,ac] (Table 2, cf. chlorostyrenes vs styrene, chlorobenzene and benzonitrile vs benzene, etc.), and remarked that the methyl radical is more polar in its addition behavior than phenyl. Later reviews[30,31,36] supported and, in part, overemphasized this point. To the contrary, recent high level ab initio studies on the addition of methyl to a variety of alkenes did not reveal a significant charge transfer in the transition state.[18,29c] Besides that, very good correlations of the calculated reaction barriers with the calculated reaction enthalpies were found, and hence, Radom et al.[18a] concluded that polar contributions to the reactivity of methyl toward alkenes are *generally* insignificant.

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Table 3. Energy Quantities for the Addition of Methyl Radicals to Alkenes (Errors Are Given in Units of the Last Digit Quoted; Numbers in Italic Letters Are from (QCISD(T)/6−311G**+ZPVE) Calculations[18a,b]

X, Y	k_{297}, M^{-1} s^{-1}	E_a, kJ/mol	h_f^0(R−H), kJ/mol[c]	h_f^0(A), kJ/mol[c]	BDE(R−H), kJ/mol	h_r, kJ/mol
H, H	3500[a]	31.4	−105(1)	52(1)	423(2)[g]	−99(4)
		35.2				*−92.3*
H, F	4200[b]	28.3[b]	−286(2)	−139(2)	410(10)[h]	−102(14)
		35.7				*−93.0*
H, Me	4300	32.3	−127(1)	20(1)	413(2)[g]	−99(4)
		33.3				*−92.4*
H, Et	6700	22.5	−147(1)	−0.4(5)	413(2)[g]	−99(4)
Me, Me	8500	28.1	−154(1)	−17(1)	404(2)[g]	−98(4)
Me, OMe	12000	25.7[b]	−272(10) [d]	−146(5)	378(10)[i]	−113(25)
Me, OAc	12000	25.7[b]	−501(5)	−349(5)	400(8)[j]	−117(18)
H, OEt	14000	25.3[b]	−272(1)	−141(5)	387(8)[i]	−109(14)
						−92.1 (OH)
H, OAc	14000	23.9	−454(5)	−315(5)	406(8)[j]	−98(18)
H, Cl	20000	23.9[b]	−132(1)	23(2)	411(8)[k]	−109(11)
		28.5				*−105.0*
H, SiMe$_3$	23000	20.8	−261(10)[d]	−123(5)	402(8)[j]	−101(23)
		29.8(SiH$_3$)				*−101.1*
Me, Cl	35000	22.5[b]	−161(8)	−21(5)	406(10)[k]	−99(23)
H, Br	90000[b]	20.2[b]	−85(1)	79(2)	403(5)[n]	−126(8)
H, Ph	260000	19.9	+8(1)	148(1)	357(6)[j]	−148(8)
Me, Ph	310000	18.9	−17(1)	113(5)	353(8)[j]	−142(14)
Cl, Cl	320000	19.1	−151(8)[d]	2(1)	393(6)[j]	−125(15)
H, CO$_2$Me	340000	16.9[b]	−452(5)	−312(5)	385(15)[l]	−120(25)
Me, CO$_2$Me	490000	18.2	−476(6)[d]	−348(5)	379(15)[l]	−114(26)
H, CN	610000	15.3[b]	+34(1)[e]	184(5)	376(9)[m]	−139(15)
		20.4				*−127.7*
H, CHO	740000	15.0[b]	−208(2)	−77(5)	372(11)[o]	−124(18)
		24.1				*−119.6*
Me, CN	760000	16.9	+5(5)	130(5)	362(8)[m]	−128(18)
Ph, Ph	780000	11.3	+91(12)[f]	246(4)	339(6)[j]	−181(22)

[a] Per CH$_2$ group. [b] Calculated from k_{338} (Table 2) or k_{297} (for E_a see Table 1) and log A = 8.6. [c] Data without comments are from the standard reference.[37] When no errors were available the error was set to 5 kJ/mol. [d] From h_f^0(Me$_2$CHOMe) = (−252.0 ± 1.0) kJ/mol, h_f^0(MeCH$_2$SiMe$_3$) = −241.0 kJ/mol, h_f^0(MeCHCl$_2$) = (−131 ± 3) kJ/mol, h_f^0(MeCHF$_2$) = (−501 ± 6) kJ/mol, h_f^0(Me$_2$CHCO$_2$Me) = (−456 ± 1) kJ/mol and the increment of (−20 ± 5) kJ/mol for replacement of one Me- by an Et-group, as derived from related pairs found in ref.[37] [e] Rakus, K.; Verevkin, S. P.; Beckhaus, H.-D.; Rüchardt, C. *Chem. Ber.* **1994**, *127*, 2225. [f] From h_f^0 = (140 ±3) kJ/mol for C$_6$H$_5$CH$_2$C$_6$H$_5$ and the increment of (−49 ± 1) kJ/mol for replacement of an H-atom by an Et-group, as derived from CH$_2$Me$_2$ and EtCHMe$_2$.[37] [g] Recommended values for BDE(Me$_3$C−H), BDE(H−CHMe$_2$), and BDE(H−CH$_2$Me).[35] [h] BDE(CH$_3$CHF−H).[38] [i] BDE (MeCHOEt-H)[39] incremented for Me$_2$COEt-H from ΔBDE (HOCHCH$_3$−H/HOCMe$_2$−H) = −9 kJ/mol.[40] [j] BDE(H−CH$_2$OCOPh), BDE(Me$_3$SiCH$_2$−H), BDE(CHCl$_2$CCl$_2$−H), BDE(PhCMeH−H) and BDE(PhCMe$_2$−H),[41] for H, OAc, and Me$_3$SiCHEt-H incremented by ΔBDE (AlkCHMe-H/AlkCH$_2$−H) = (−13 ± 3) kJ/mol, for Me, OAc by ΔBDE(AlkCMe$_2$−H/AlkCH$_2$−H) = (−19 ± 3) kJ/mol.[35] [k] BDE(CH$_3$CHCl−H) and ΔBDE(CH$_3$CHCl−H/CH$_2$Cl−H) = (−5 kJ/mol).[42a] BDE = (401 ± 4) is reported in ref 42b. [l] BDE(H−CH$_2$CO$_2$CH$_3$)[43] incremented by ΔBDE(AlkCHMe-H/AlkCH$_2$−H) =(−13 ± 3) kJ/mol and ΔBDE(AlkCMe$_2$−H/AlkCH$_2$−H) = −(19 ± 3) kJ/mol.[35] [m] BDE(Me$_2$CCN−H) and BDE(MeCHCN−H).[44] [n] BDE(MeCHBr−H).[45] [o] BDE(OHCCH$_2$−H)[46] incremented by ΔBDE(AlkCHMe-H/AlkCH$_2$−H) = (−13 ± 3) kJ/mol.[35]

Here, we again consider the correlations between the experimental activation energies and log(k) and the reaction enthalpies, the alkene ionization energies, and electron affinities for the addition of methyl to mono- and 1,1-disubstituted alkenes based on the now available larger data set. 1,1-Difluoroethene is not included in the analysis because there is addition to the CF$_2$ carbon, also.[27,31]

The alkene ionization energies and electron affinities were taken from ref 37 or the literature quoted in our earlier work.[17] However, the reaction enthalpies are not available from experiment and were determined indirectly. By considering the overall reaction

$$CH_4 + CH_2{=}CXY \rightarrow CH_3 + H + CH_2{=}CXY \rightarrow$$
$$CH_3CH_2CXY + H \rightarrow CH_3CH_2CHXY$$
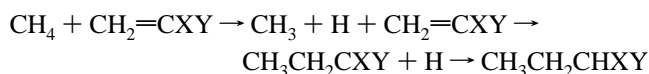
one obtains for the reaction enthalpy

$$h_r = h_f(CH_3CH_2CHXY) - h_f(CH_2{=}CXY) - h_f(CH_4) +$$
$$BDE(CH_3CH_2CHXY) - BDE(CH_4) \quad (11)$$

With this equation we estimated h_r for 300 K from the best available heats of formation and bond dissociation energies

(37) Lias, S. G.; Bartmess, J. E.; Liebman, J. F.; Holmes, J. L.; Levin, R. D.; Mallard, W. G. *J. Phys. Chem. Ref. Data* **1988**, *17*, Suppl. 1.

BDE. For methane $h_f^0 = -74.5(5)$ kJ/mol[37] and BDE = 439(1) kJ/mol[35] were used. Table 3 gives the energy quantities needed and the reaction enthalpies including all errors, with footnotes referring to the details of the determination. Small differences to enthalpies given earlier[17i] are due to the inclusion of more precise recent data. Table 3 also gives the enthalpies and the reaction barriers calculated by Radom et al.[18a] with a refined quantum chemical method. Considering the appreciable errors, the experimental and theoretical reaction enthalpies agree fairly well though the calculated exothermicities appear on average somewhat lower.

Figures 5 and 6 show the activation energies and log(k(297)/ M^{-1} s^{-1}) plotted versus the reaction enthalpies of Table 3. Obviously, the rate constants do increase and the activation energies decrease with increasing exothermicity of the addition but the correlations are weak. The straight lines are represented by

$$E_a/\text{kJ/mol} = 44.8(46) + 0.195(39)h_r/\text{kJ/mol}$$
$$R^2 = 0.560 \quad (12)$$

$$\log(k_{297}/\text{M}^{-1}\,\text{s}^{-1}) = 0.97(74) - 0.032(6)h_r/\text{kJ/mol}$$
$$R^2 = 0.569 \quad (13)$$

Interestingly, the slopes of the linear correlations are similar to those found for radicals with a more clear-cut enthalpy
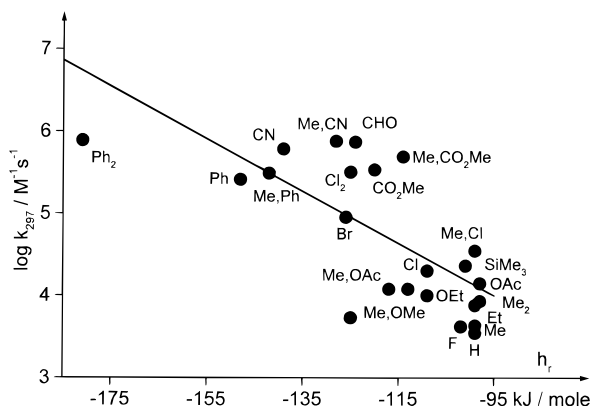
Figure 5. Rate constants for the addition of methyl to mono- and 1,1-disubstituted alkenes plotted vs the reaction enthalpy. Symbols denote the substituents, H = ethene.
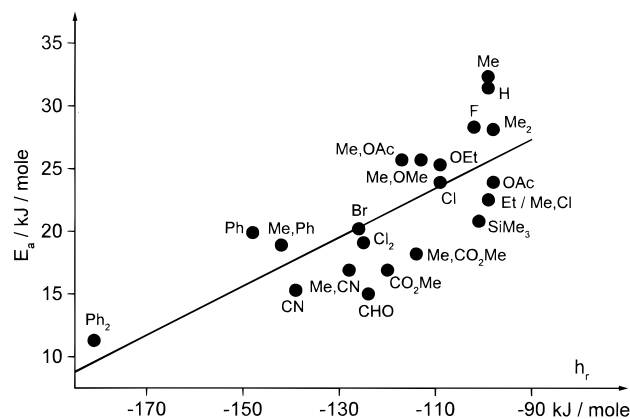
Figure 6. Activation energies for the addition of methyl to mono- and 1,1-disubstituted alkenes plotted vs the reaction enthalpy. Symbols denote the substituents, H = ethene.

Figure 7. Rate constants for the addition of methyl to mono- and 1,1-disubstituted alkenes plotted vs the alkene electron affinities. Symbols denote the substituents, H = ethene.

Figure 8. Activation energies for the addition of methyl to mono- and 1,1-disubstituted alkenes plotted vs the alkene electron affinities. Symbols denote the substituents, H = ethene.

control, as, for $\log(k)$, -0.037 for cyanomethyl, -0.039 for *tert*-butoxycarbonylmethyl, -0.039 for 2-cyano-2-propyl, and -0.045 for benzyl.[17a] This clearly suggests that the enthalpy effect operates also for methyl.

In comparison, the calculated data of Radom et al. for 10 alkenes[18] gave the much better correlation

$$E_a/\text{kJ/mol} = 72.6 + 0.41 h_r/\text{kJ/mol} \qquad R^2 = 0.973 \quad (14)$$

with a considerably larger slope than (12), However, restricting the analysis of our data to alkenes covered in the theoretical work (X = H, F, Cl, Me, CN, CHO, SiH$_3$ (here SiMe$_3$), and OH (here OEt)) we obtain

$$E_a/\text{kJ/mol} = 67.2(116) + 0.39(10) h_r/\text{kJ/mol} \qquad R^2 = 0.702 \quad (15)$$

which is within the error limits identical with (14), i.e., there is a good general agreement between the calculated and the experimental barriers. Hence, the larger scatter in our Figure

6 as compared to Radom's plots is at least partly due to our larger set of alkenes.

Figure 5 and Tables 1 and 2 also show that the methyl radical reacts as fast or even faster with strongly electron deficient alkenes than with styrene and α-methyl styrene, which were not covered by Radom.[18] We think that this must be due to a nucleophilic polar effect. It is weaker than for hydroxymethyl, 2-hydroxy-2-propyl, and *tert*-butyl radicals, which add to electron deficient alkenes even faster than to 1,1-diphenylethene.

In the analysis for polar effects, correlations of $\log(k)$ or E_a vs the alkene ionization energies gave a complete scatter. This was expected since the methyl radical has never been found electrophilic. On the other hand, the correlations with the electron affinities are very reasonable and are shown in Figures 7 and 8.

The straight lines are

$$E_a/\text{kJ/mol} = 15.7(10) - 5.7(7)\text{EA/eV} \qquad R^2 = 0.778 \quad (16)$$

$$\log(k_{297}/\text{M}^{-1}\,\text{s}^{-1}) = 5.78(13) + 0.97(10)\text{EA/eV}$$
$$R^2 = 0.854 \quad (17)$$

In comparison to more clearly nucleophilic radicals[17] the slopes are smaller. Their ordering, for $\log(k)$, cf. 0.97 vs 1.53,

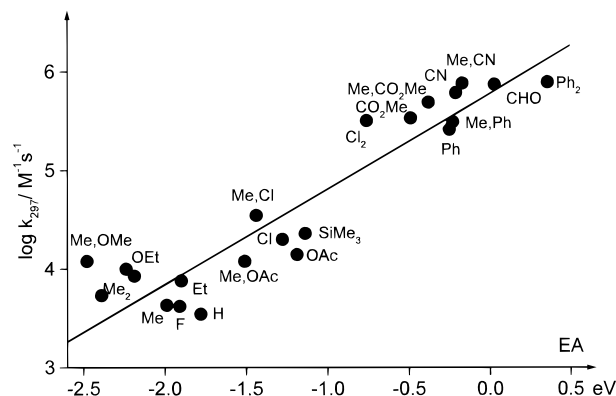(38) Martell, J. M.; Boyd, R. J.; Shi, Z. *J. Phys. Chem.* **1993**, *97*, 7208 and references therein.

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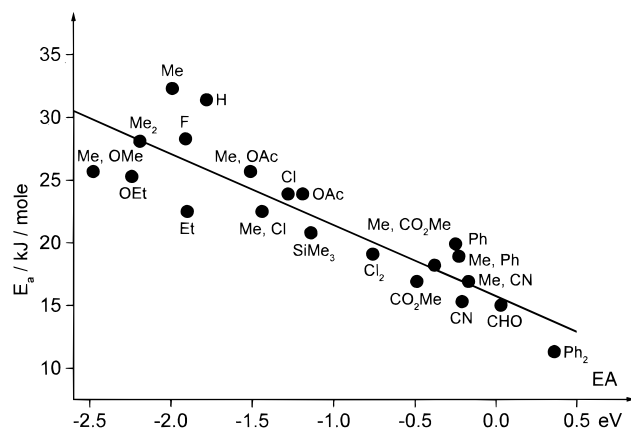
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1.61, and 2.81 for methyl, hydroxymethyl, *tert*-butyl, and 2-hydroxy-2-propyl, respectively, reflects the ordering of the radical ionization energies of 9.84 vs 7.5, 6.7, and 6.5 eV, respectively. Restricting the number of data points as above to the alkenes covered by Radom one obtains

$$E_a/\text{kJ/mol} = 14.7(22) - 7.1(14)\text{EA/eV} \qquad R^2 = 0.801 \quad (18)$$

and this is again similar to the theoretically found correlation,[18a,b] namely

$$E_a/\text{kJ/mol} = 24.9 - 5.43 \cdot \text{EA/eV} \qquad R^2 = 0.825 \quad (19)$$

It is known that the alkene electron affinities correlate with the reaction enthalpies,[17,18] and, hence, the correlations with EA may deceive and may be caused by the reaction enthalpy effect, only. Nevertheless, the behavior of methyl toward the strongly electron deficient alkenes in comparison to the styrenes forces us to conclude that the addition to alkenes is not alone influenced by the reaction enthalpy but also by a nucleophilic polar effect, in keeping with all earlier notions. This is also supported by the rate data for addition to substituted benzenes since chloro-, bromo-, and cyano-substituted compounds react faster than the parent benzene whereas anisol reacts slower. The same is seen for higher condensed aromatic compounds, and we deem it very unlikely that these substituent effects are caused by variations in the stabilization of the reactants or the cyclohexadienyl radicals resulting from the addition. A full discussion of these cases is beyond the scope of this work, however, and requires estimations of reaction enthalpies for which there is no safe basis yet.

As mentioned above, there is no large discrepancy between Radom's theoretical[18] and our experimental results though the conclusions differ and subtle differences remain. In this respect, it should be kept in mind that our conclusion of an addition behavior mainly controlled by the reaction enthalpy but noticably modulated by nucleophilic polar effects is based on data obtained for liquid solutions. On the other hand, the calculated reaction barriers, enthalpies, and transferred charges are for isolated reactants at 0 K, i.e., gas-phase conditions. Hence, it may be significant that Radom's highest level calculations give barriers which are on the average slightly higher than our activation energies (Table 3), and that the experimental activation energies may be larger for the gas than for the liquid phase (vide supra). Therefore, there may be a real difference between the two phases. In the liquid-phase solvation effects may lower the energies of the excited configurations such as the charge-transfer configurations and increase their contribution to the transition state. Hence, the polar effects may in fact be stronger for the liquid phase, which would be in keeping with a slight solvent effect, though the extensive work of Tedder et al.[30] on the addition of methyl to fluoroethenes indicates that polar effects do exist also in gases.

Supporting Information Available: Three tables with magnetic properties of the adduct radicals, additional methyl affinities, and their conversion to absolute rate constants and a comparison of gas phase and solution rate data (6 pages). See any current masthead page for ordering and Internet access instructions.

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