J. Am. Chem. Soc. **1996,** *118,* 437−439

Absolute Rate Constants for the Addition of Methyl Radicals to Alkenes in Solution: New Evidence for Polar Interactions

Torsten Zytowski and Hanns Fischer*

Contribution from the Physikalisch-Chemisches Institut, Universität Zürich,
Winterthurerstrasse 190, CH-8057 Zürich, Switzerland

Received September 7, 1995⊗

Abstract: Absolute rate constants are reported for the addition of the methyl radical to 20 monosubstituted and 1,1-disubstituted alkenes at room temperature in liquid solution. They increase with increasing exothermicity of the addition and are enhanced by strong nucleophilic polar effects for electron-deficient alkenes. This agrees with conclusions derived from earlier relative rate data but disagrees with a general insignificance of polar effects predicted by *ab initio* calculations.

The rate constants for the addition of carbon-centered radicals to alkenes $CH_2{=}CXY$ vary strongly with radical and alkene substitution.[1] This is generally ascribed to a dependence of the activation barrier on the reaction enthalpy and to stabilizing polar interactions in the transition state. Particularly large polar effects are known for the nucleophilic *tert*-butyl and α-hydroxyalkyl radicals[2] and for the electrophilic perfluoroalkyl[3] and dicyanomethyl[4] species. The addition rates of other radicals follow the enthalpy variation and exhibit only weak nucleophilic[5] ($(CH_3)_2\dot{C}CN$, benzyl, and cumyl) or electrophilic[6] ($\dot{C}H_2CO_2C(CH_3)_3$, $\dot{C}H_2CN$) effects.

For the parent methyl radical controversial views have been expressed. Szwarc's rate constants for addition[7] measured relative to the hydrogen abstraction from isooctane at 65 °C indicate nucleophilic polar effects since methyl reacts faster with electron-deficient alkenes than with styrenes. In the methylation of protonated heteroaromatic bases Minisci et al.[8] also found a nucleophilic addition behavior. However, in both cases the polar effects are much weaker than for more easily oxidizable radicals, e.g. *tert*-butyl. To the contrary, *ab initio* studies of transition states for methyl additions did not reveal substantial charge transfer.[9] Instead, Fueno et al.[10] found a linear barrier−enthalpy correlation for six alkenes ($CH_2{=}CHX$, X = OCH_3, CH_3, H, CO_2H, CN, C≡CH, UHF 3-21G). Using the advanced QCISD-(T)/6-311G**//UHF/6-31G*+ZPVE level the same was found by Radom et al.[11] for ten alkenes ($CH_2{=}CHX$, X = H, CH_3, NH_2, OH, F, SiH_3, Cl, CN, CHO, NO_2, $E_a = 72.6 + 0.41H_r$, in $kJ{\cdot}mol^{-1}$, $R^2 = 0.973$). These authors concluded[11a] that polar contributions to the reactivity of methyl toward alkenes are *generally insignificant*, and that the reaction enthalpy is the dominant factor.

To provide a larger basis for discussion we have now determined absolute rate constants for the addition of the methyl radical to 20 monosubstituted and 1,1-disubstituted alkenes in liquid solution at 24 °C. As in earlier work[2,5,6] kinetic ESR spectroscopy with intermittent photochemical radical generation was applied. The radicals were produced by photolysis (260 nm ≤ λ ≤ 340 nm) of oxygen-free solutions of dicumyl peroxide (Aldrich, repeatedly recrystallized from methanol, 0.022 M) in a flow system. The primary cleavage (eq 1) is followed by a fast ($k_2 > 10^5\ s^{-1}$) fragmentation[12] which renders the formation of methyl instantaneous on our experimental time scale (20 μs to 20 ms).

$$C_6H_5(CH_3)_2COOC(CH_3)_2C_6H_5 \xrightarrow{h\nu} 2C_6H_5(CH_3)_2C\dot{O} \qquad (1)$$

$$C_6H_5(CH_3)_2C\dot{O} \rightarrow C_6H_5COCH_3 + \dot{C}H_3 \qquad (2)$$

Since the product acetophenone may sensitize[13] the cleavage in eq 1 it was added deliberately (0.033 M). For the solvent chosen, 1,1,2-trichloro-1,2,2-trifluoroethane (Johnson Matthey Alfa Products, >99.8%), methyl was the only radical detectable during continuous photolysis. In the absence of alkenes it

---

⊗ Abstract published in *Advance ACS Abstracts,* December 15, 1995.

[1] For reviews, see: (a) Giese, B. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 573 (73). (b) Tedder, J. M. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 401.

[2] (a) Münger, K.; Fischer, H. *Int. J. Chem. Kinet.* **1985**, *17*, 809. (b) Fischer, H. In *Substituent Effects in Radical Chemistry*; Viehe, H. G., Janousek, Z., Mérényi, R., Eds.; Reidel: Dordrecht, 1986. (c) Salikhov, A.; Fischer, H. *Appl. Magn. Reson.* **1993**, *5*, 445. (d) Héberger, K.; Fischer, H. *Int. J. Chem. Kinet.* **1993**, *25*, 913. (e) Wu, J. Q.; Fischer, H. *Int. J. Chem. Kinet.* **1995**, *27*, 167.

[3] (a) Avila, D. V.; Ingold, K. U.; Lusztyk, J.; Dolbier, W. R.; Pan, H.-Q. *J. Am. Chem. Soc.* **1993**, *115*, 1577. (b) Avila, D. V.; Ingold, K. U.; Lusztyk, J.; Dolbier, W. R.; Pan, H.-Q. *J. Am. Chem. Soc.* **1994**, *116*, 99. (c) Rong, X. X.; Pan, H.-Q.; Dolbier, W. R.; Smart, B. E. *J. Am. Chem. Soc.* **1994**, *116*, 4521.

[4] Riemenschneider, K.; Bartels, H. M.; Dornow, R.; Drechsel-Grau, E.; Eichel, W.; Luthe, H.; Michaelis, Y. M.; Boldt, P. *J. Org. Chem.* **1987**, *52*, 205.

[5] (a) Héberger, K.; Fischer, H. *Int. J. Chem. Kinet.* **1993**, *25*, 249. (b) Walbiner, M.; Wu, J. Q.; Fischer, H. *Helv. Chim. Acta* **1995**, *78*, 910.

[6] Wu, J. Q.; Beranek, I.; Fischer, H. *Helv. Chim. Acta* **1995**, *78*, 194.

[7] (a) Leavitt, F.; Levy, M.; Szwarc, M.; Stannett, V. *J. Am. Chem. Soc.* **1955**, *77*, 5493. (b) Szwarc, M. *J. Polym. Sci.* **1955**, *16*, 367. (c) Smid, J.; Szwarc, M. *J. Am. Chem. Soc.* **1956**, *78*, 3322. (d) Buckley, R. P.; Szwarc, M. *J. Am. Chem. Soc.* **1956**, *78*, 5696. (e) Buckley, R. P.; Leavitt, F.; Szwarc, M. *J. Am. Chem. Soc.* **1956**, *78*, 5557. (f) Buckley, R. P.; Szwarc, M. *Proc. R. Soc. (London)* **1957**, *A240*, 396. (g) Herk, L.; Stefani, A.; Szwarc, M. *J. Am. Chem. Soc.* **1961**, *83*, 3008.

[8] Minisci, F.; Mondelli, R.; Gardini, G. P.; Porta, O. *Tetrahedron* **1972**, *28*, 2403.

[9] (a) Arnaud, R.; Barone, V.; Olivella, S.; Solé, A. *Chem. Phys. Lett.* **1985**, *118*, 573. (b) Arnaud, R.; Subra, R.; Barone, V.; Lelj, F.; Olivella, S.; Solé, A.; Russo, N. *J. Chem. Soc., Perkin Trans. 2* **1986**, 1517. (c) Houk, K. N.; Paddon-Row, M. N.; Spellmeyer, D. C.; Rondan, N. G.; Nagase, S. *J. Org. Chem.* **1986**, *51*, 2874. (d) Gonzalez, C.; Sosa, C.; Schlegel, H. B. *J. Phys. Chem.* **1989**, *93*, 2435.

[10] Fueno, T.; Kamachi, M. *Macromolecules* **1988**, *21*, 908.

[11] (a) Wong, M. W.; Pross, A.; Radom, L. *J. Am. Chem. Soc.* **1993**, *115*, 11050. (b) Wong, M. W.; Pross, A.; Radom, L. *Isr. J. Chem.* **1993**, *33*, 415. (c) Wong, M. W.; Pross, A.; Radom, L. *J. Am. Chem. Soc.* **1994**, *116*, 6284.

[12] Avila, D. V.; Brown, C. E.; Ingold, K. U.; Lusztyk, J. *J. Am. Chem. Soc.* **1993**, *115*, 466.

[13] Walling, C.; Gibian, M. J. *J. Am. Chem. Soc.* **1965**, *87*, 3413.

0002-7863/96/1518-0437$12.00/0

Table 1. Absolute and Relative Rate Constants (M^{-1} s^{-1}) for Methyl Addition to Alkenes $CH_2{=}CXY$, Alkene Electron Affinities (EA/eV) and Ionization Energies (IP/eV), Estimated Reaction Enthalpies (H_r), and Activation Energies (kJ mol^{-1})

X, Y	k	k_{rel}[a]	EA[b]	IP[b]	H_r[b]	E_a
H, H[c]	3500	17	−1.78	10.5	−98	28.2
calcd[d]					*−92.3*	*35.2*
H, Me	4300	22	−1.99	9.5	−104	27.7
calcd[d]					*−92.4*	*33.3*
H, Et	7600	27	−1.90	9.6	−104	26.3
Me, Me	8500	36	−2.19	9.6	−100	26.0
H, OAc	10000	37	−1.19	9.2	−97	25.6
Me, OMe	12000		−2.48	8.6	−109	25.1
Me, OAc	12000		−1.51	9.1	−117	25.1
H, OEt	14000		−2.24	8.8	−106	24.8
calcd[d,e]					*−92.1*	*34.7*
H, Cl	20000		−1.28	10.0	−106	23.9
calcd					*−105*	*28.5*
H, $SiMe_3$	24000		−1.14	9.5	−102	23.4
calcd[d,f]					*−101*	*29.8*
Me, Cl	35000		−1.44	9.8	−96	22.5
Cl, Cl	230000		−0.76	9.8	−119	17.9
H, C_6H_5	260000	792	−0.25	8.4	−143	17.5
Me, C_6H_5	300000	926	−0.23	8.2	−139	17.2
H, CO_2Me	340000	1030	−0.49	9.9	−118	16.9
Me, CO_2Me	490000	1440	−0.38	9.7	−130	16.0
Me, CN	490000	2120	−0.17	10.4	−127	16.0
H, CN	610000	1730	−0.21	10.9	−139	15.4
calcd[d]					*−127.7*	*20.4*
C_6H_5, C_6H_5	690000	1590	+0.36	8.0	−153	15.1
H, CHO	740000	1900	+0.03	10.1	−118	15.0
calcd[d]					*−119.6*	*24.1*

[a] Reference 7, 65 °C. [b] References given in ref 2e. [c] Per CH_2 group. [d] QCISD(T)/6-113G**//UHF/6-31G*+ZPVE level.[11a] [e] Calculated for Y = OH. [f] Calculated for Y = SiH_3.

decayed by second-order kinetics ($\tau_2 \approx 220$ μs) slightly perturbed by a first- or pseudo-first-order ($\tau_{10} = (10 \pm 2)$ ms) which we attribute to reactions with solvent and/or the starting compounds. From the steady-state radical concentration and the second-order lifetime the rate constant for the self-termination of methyl was obtained as $2k_t = (1.6 \pm 0.2) \times 10^{10}$ M^{-1} s^{-1}, and is as expected for a diffusion-controlled process. In the presence of alkenes **A** the pseudo-first-order contribution increased as $\tau_1^{-1} = \tau_{10}^{-1} + k[\mathbf{A}]$, i.e. methyl reacts with the alkenes. It is known[14] that this involves the selective addition to the unsubstituted carbon atom of $CH_2{=}CXY$, and the nature of the adduct radicals $CH_3CH_2\dot{C}XY$ was reensured here for a few cases only. The rate constants for the addition were obtained from the slopes of the linear relations between τ_1^{-1} and [**A**], and for each alkene 4 to 6 concentrations and 20 to 40 individual kinetic runs were employed. The average values given have estimated errors lower than ±20%.

Table 1 shows the results together with Szwarc's relative data,[7] the alkene electron affinities (EA) and ionization energies (IP), and the reaction enthalpies (H_r) for the addition. The latter are derived from experimental bond dissociation energies and molecular heats of formation as described in detail earlier[2e] and are believed to be correct to about 5 kJ mol^{-1}. In the last column activation energies are listed which were estimated from the rate constants with a common frequency factor $\log(A/M^{-1}\,s^{-1}) = 8.5$. This is the average of four average frequency factors established for the addition of other primary alkyl radicals to the same alkenes[2e,5b,6] and is close to the preferred gas-phase value[15] of $\log(A/M^{-1}\,s^{-1}) = 8.3$. For comparison Table 1 also contains Radom's *ab initio* enthalpies and barriers.[11a,b]

So far, only a few indirect measurements of methyl addition rate constants are available. Thomas[16] reported k = 2 450, 5 300, 30 000, and 39 000 M^{-1} s^{-1} for the addition to ethene, propene, 1-butene, and 2-methylpropene, respectively, in water at 25 °C. The first two values agree fairly well with our results but the latter two appear high. The preferred Arrhenius parameters for the gas-phase addition[15] lead to a low k_{300} = 400 M^{-1} s^{-1} for ethene (statistically corrected), but somewhat higher values are also available.[17] Finally, with the only exception of 2-cyanopropene, our data correlate extremely well with Szwarc's relative rate constants[7] at 65 °C. Hence, all earlier findings support the present rate constants and their ordering with the alkene substituents to a fair extent.

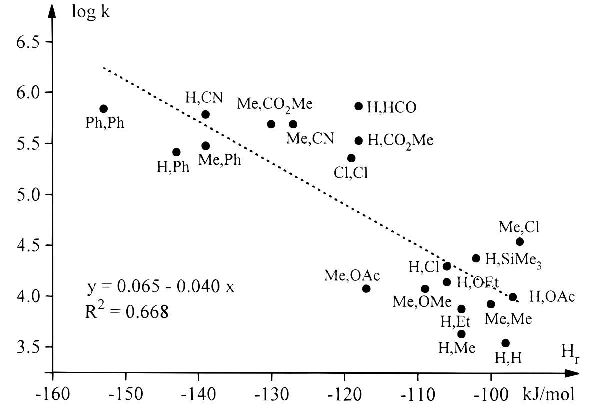

Figure 1. Correlation of log *k* (24 °C) for the addition of the methyl radical to alkenes $CH_2{=}CXY$ with the reaction enthalpy H_r.

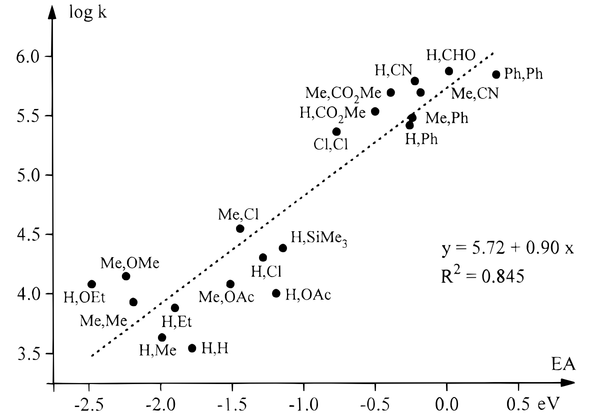

Figure 2. Correlation of log *k* (24 °C) for the addition of the methyl radical to alkenes ($CH_2{=}CXY$) with the alkene electron affinity EA.

To analyze for enthalpic and polar substituent effects it is common to seek correlations of log *k* with either H_r or EA and IP.[2−6,11] Here, we do not find a significant dependence on IP. Hence, methyl does not express electrophilic polar effects as it does not react particularly fast with low IP alkenes. On the other hand, the correlations with H_r (Figure 1) and EA (Figure 2) are significant. Since H_r and EA themselves correlate[5,6,11] for many alkenes it is difficult to assess the dominating factor. However, a comparison with other radicals clearly shows that the rate constants for the addition of methyl to alkenes (a) grossly increase with increasing reaction exothermicity and are (b) strongly enhanced by nucleophilic effects for electron-deficient alkenes. The strong influence of H_r is revealed by the close similarity of the linear correlation given in Figure 1 with that found for the much less reactive 2-cyano-2-propyl

---

[14] Fischer, H.; Giacometti, G. *J. Polym. Sci. C* **1967**, *16*, 2763.

[15] (a) Baulch, D. L.; Cobos, C. J.; Cox, R. A.; Enser, C.; Frank, P.; Just, T.; Kerr, J. A.; Pilling, M. J.; Troe, J.; Walker, R. W.; Warnatz, J. *J. Phys. Chem., Ref. Data* **1992**, *21*, 411. (b) Holt, P. M.; Kerr, J. A. *Int. J. Chem. Kinet.* **1977**, *9*, 185.

[16] Thomas, J. K. *J. Phys. Chem.* **1967**, *71*, 1919.

[17] Cvetanovic, R. J.; Irwin, R. S. *J. Chem. Phys.* **1967**, *46*, 1694.

radical[5a] (log $k = 0.000 - 0.039H_r$, $R^2 = 0.850$) which does not exhibit polar effects. Furthermore, the slope is very similar to those obtained for benzyl (−0.045), cyanomethyl (−0.039) and *tert*-butoxycarbonylmethyl (−0.037), i.e. radicals for which the reaction enthalpy is also the dominant factor.[5b,6] We note here that the linear correlation between log k and H_r for methyl corresponds to a linear relation of the activation energy E_a and H_r with a slope of 0.23. The strong nucleophilic rate enhancements (b) are evidenced in Figure 1 by the marked positive deviations of log k for the chloroalkenes, the acrylates, the acrylonitriles, and acrolein from the average correlation and are supported by the correlation of Figure 2. In comparison to the other radicals with dominating enthalpy effects the enhancements amount to factors of 5−20. As already noticed by Szwarc[7] they cause a similar fast or faster addition to the electron-deficient alkenes than to the styrenes. In comparison to *tert*-butyl,[2a−c] 2-hydroxy-2-propyl,[2d] and hydroxymethyl[2e] the methyl radical is clearly less nucleophilic, however. In keeping with their ionization energies[18] of 6.4−7.6 eV which are much lower than that of methyl (9.8 eV), the slopes of their log k *vs* EA correlations are also steeper, and they react by one to two orders of magnitude faster with acrylonitriles or acrolein than with the styrenes.

In principle our results confirm the theoretical prediction[9,10,11] of a strong influence of the reaction enthalpy on the reaction barrier for methyl additions to alkenes. However, the dependence is weaker than calculated.[11] They clearly disagree with a *general insignificance* of polar contributions[11a,b] but support the earlier notations[7,8] of a nucleophilic addition behavior to electron-deficient alkenes which is weaker than that expressed by other alkyl radicals. A direct comparison of theoretical and experimental reaction enthalpies and barriers (Table 1) has to allow for the accuracy of the data of both sets of an estimated 5−10 kJ mol^{-1}. Also, the theoretical values refer to 0 K and gas phase and the experimental values to 24 °C and solutions with solvent effects of unknown magnitude. Hence, the overall agreement between theory and experiment is acceptable. Nevertheless, there are differences in the trends which suggest that even the most advanced *ab initio* methods may underestimate the radical stabilization by methyl, alkoxy, and cyano groups[19] and the polar effects of substituents on addition barriers.

Studies on the temperature dependence of methyl addition rates are in progress.

Acknowledgment. We acknowledge useful discussions and the exchange of results with Professor Leo Radom, advice on gas-phase data from Professor J. A. Kerr, and financial support from the Swiss National Foundation for Scientific Research.

JA953085Q

---

[18] 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.

[19] Bordwell, F. G.; Zhang, X.-M.; Alnajjar, M. S. *J. Am. Chem. Soc.* **1992**, *114*, 7623.