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Are Polar Interactions Important in the Addition of Methyl Radical to Alkenes?

Ming Wah Wong,[*,1a,b] Addy Pross,[*,1c,d] and Leo Radom[*,1a]

Research School of Chemistry
Australian National University
Canberra, ACT 0200, Australia
Department of Chemistry
University of Queensland
Brisbane, QLD 4072, Australia
School of Chemistry
University of Sydney
Sydney, NSW 2006, Australia

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The importance of polar effects in the addition of methyl radical to alkenes has been emphasised for many years.[2,3] Both older experimental studies[3] and more recent theoretical studies[4,5] have led to the conclusion that the methyl radical is nucleophilic in character. Evidence for this nucleophilic character has largely rested on the observation that electron-withdrawing groups on the alkene substrate enhance the rate of methyl addition. Consequently, the methyl radical has been utilized in theoretical studies as a model for a nucleophilic radical.[4]

We report here results of a theoretical study of methyl radical addition to a series of substituted alkenes, studied with use of quantitative ab initio molecular calculations[7] together with application of the curve-crossing model.[8,9] We reach the surprising conclusion that *polar contributions to the reactivity of the methyl radical toward alkenes are generally insignificant, and reaction exothermicity is the dominant influencing factor.*

High-level ab initio calculations[7] were carried out using the GAUSSIAN 92 series of programs[10] for the reactants, products, and transition structures for the series of reactions

$$CH_3^{\bullet} + CH_2{=}CHX \rightarrow CH_3CH_2CHX^{\bullet} \qquad (1)$$

with X = H, CH_3, NH_2, OH, F, SiH_3, Cl, CN, CHO, and NO_2. Reaction barriers and enthalpies were obtained at the QCISD(T)/6-311G**//HF/6-31G*+ZPVE level[11] by using an additivity approximation.[12] The extent of charge transfer between the radical and the alkene was calculated by using the Bader approach and the PROAIM program.[13] Adiabatic ionization energies (I) and electron affinities (A) for the methyl radical and the set of alkenes $CH_2{=}CHX$ were obtained at the G2(MP2) level of theory.[14] Comparative experimental results are taken largely from the compendium of Lias et al.[15] A summary of the results is presented in Table I. Full details will be reported elsewhere.[16]

The possible influence of reaction enthalpy on the reactivity of methyl radical with alkenes may be explored by plotting the reaction barrier against exothermicity (Figure 1). An excellent correlation is observed ($R^2 = 0.973$) with a slope of 0.41, consistent with the results of a previous study.[6b] *The excellent correlation suggests that reaction thermodynamics is the factor that dominates the rate of methyl radical addition to alkenes.*

If polar effects are important in determining reactivity, then these are expected to be governed by the relative magnitudes of $I_{rad} - A_{alk}$ (representing charge transfer from the radical to the alkene, denoted D^+A^-) and $I_{alk} - A_{rad}$ (denoted D^-A^+).[17] We observe (Table I) that in most cases, including the unsubstituted case, the energy of the charge-transfer state D^+A^- is *higher* than that of the charge-transfer state D^-A^+. This is consistent with an assessment based on calculated charges in the transition states, also included in Table I. Thus, for X = F, H, OH, CH_3, SiH_3, and NH_2, methyl radical is predicted to be an electron acceptor and for X = Cl there is no charge transfer, while only for X = CHO, NO_2, and CN does methyl act as a weak donor. Both the $I - A$ analysis for separated reactants and the charge analysis in the transition state therefore suggest that *methyl radical does not display general nucleophilic behavior.*

What, then, is the significance of the experimental observation that electron-withdrawing substituents in the alkene generally lead to lower reaction barriers? The answer is that π-electron-accepting groups such as CHO, NO_2, and CN tend to increase reaction exothermicity, in part because the product radical $CH_3CH_2CHX^{\bullet}$ formed from the addition of methyl to the alkene is stabilized by such α-substituents, as found also in a study of the reactions of cyanopropyl radical with alkenes.[2c] Thus, *π-electron-accepting groups enhance reactivity because these groups tend to increase reaction exothermicity and not because of induced polar character in the transition state.*

The above conclusions are reinforced by a curve-crossing analysis. According to the curve-crossing model,[8,9] the wave function that describes the ground-state reaction surface for radical addition to an alkene may be built up from the electronic configurations, DA, D^3A^*, D^+A^-, and D^-A^+, whose energies are plotted in Figure 2. The initial energy of D^3A^* is estimated to be in the range 340–440 kJ mol^{-1} (3.5–4.5 eV).[18] Adiabatic

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[1] (a) Australian National University. (b) University of Queensland. (c) University of Sydney. (d) Permanent address: Ben-Gurion University of the Negev, Beer Sheva, Israel.

[2] For reviews, see: (a) Giese, B. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 753. (b) Tedder, J. M. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 401. For a recent thorough analysis, see: (c) Heberger, K.; Fischer, H. *Int. J. Chem. Kinet.* **1993**, *25*, 249.

[3] (a) Szwarc, M. *J. Polym. Sci.* **1955**, *16*, 367. (b) Leavitt, F.; Levy, M.; Szwarc, M. *J. Am. Chem. Soc.* **1955**, *77*, 5493. (c) Bader, A. R.; Buckley, R. P.; Leavitt, F.; Szwarc, M. *J. Am. Chem. Soc.* **1957**, *79*, 5621.

[4] Zipse, H.; He, J.; Houk, K. N.; Giese, B. *J. Am. Chem. Soc.* **1991**, *113*, 4324.

[5] (a) Arnaud, R.; Subra, R.; Barone, V.; Lelj, F.; Olivella, S.; Sole, A.; Russo, N. *J. Chem. Soc., Perkin Trans. 2* **1986**, 1517. (b) Clark, T. *J. Chem. Soc., Chem. Commun.* **1986**, 1774. (c) Arnaud, R. *New J. Chem.* **1989**, *13*, 543. For additional recent computational studies on methyl radical addition to alkenes, see ref 6.

[6] (a) Houk, K. N.; Paddon-Row, M. N.; Spellmeyer, D. C.; Rondan, N. G.; Nagase, S. *J. Org. Chem.* **1986**, *51*, 2874. (b) Fueno, T.; Kamachi, M. *Macromolecules* **1988**, *21*, 908. (c) Gonzales, C.; Sosa, C.; Schlegel, H. B. *J. Phys. Chem.* **1989**, *93*, 2435; **1989**, *93*, 8388. (d) Arnaud, R.; Vidal, S. *New J. Chem.* **1992**, *16*, 471. (e) Tozer, D. J.; Andrews, J. S.; Amos, R. D.; Handy, N. C. *Chem. Phys. Lett.* **1992**, *199*, 229.

[7] Hehre, W. J.; Radom, L.; Schleyer, P. v. R.; Pople, J. A. *Ab Initio Molecular Orbital Theory*; Wiley: New York, 1986.

[8] For reviews of the curve-crossing model, see: (a) Pross, A.; Shaik, S. S. *Acc. Chem. Res.* **1983**, *16*, 363. (b) Pross, A. *Adv. Phys. Org. Chem.* **1985**, *21*, 99. (c) Shaik, S. S. *Prog. Phys. Org. Chem.* **1985**, *15*, 197. (d) Shaik, S. S.; Schlegel, H. B.; Wolfe, S. *Theoretical Aspects of Physical Organic Chemistry, The S_N2 Transition State*; Wiley: New York, 1992.

[9] For a previous application of the curve-crossing model to radical addition, see: Shaik, S. S.; Canadell, E. *J. Am. Chem. Soc.* **1990**, *112*, 1446.

[10] Frisch, M. J.; Trucks, G. W.; Head-Gordon, M.; Gill, P. M. W.; Wong, M. W.; Foresman, J. B.; Johnson, B. G.; Schlegel, H. B.; Robb, M. A.; Replogle, E. S.; Gomperts, R.; Andres, J. L.; Raghavachari, K.; Binkley, J. S.; Gonzalez, C.; Martin, R. L.; Fox, D. J.; DeFrees, D. J.; Baker, J.; Stewart, J. J. P.; Pople, J. A. *GAUSSIAN 92*; Gaussian Inc.: Pittsburgh, PA, 1992.

[11] (a) Pople, J. A.; Head-Gordon, M.; Raghavachari, K. *J. Chem. Phys.* **1987**, *87*, 5968. (b) Knowles, P. J.; Andrews, J. S.; Amos, R. D.; Handy, N. C.; Pople, J. A. *Chem. Phys. Lett.* **1991**, *186*, 130. (c) Zero-point vibrational energies (ZPVE) are HF/6-31G* values, scaled by 0.8929.

[12] $\Delta E(\text{QCISD(T)/6-311G**}) \approx \Delta E(\text{QCISD(T)/6-31G*}) + \Delta E(\text{RMP2/6-311G**}) - \Delta E(\text{RMP2/6-31G*})$.

[13] (a) Bader, R. F. W. *Atoms in Molecules. A Quantum Theory*; Oxford Press: New York, 1990. (b) Biegler-Konig, F. W.; Bader, R. F. W.; Tang, T.-H. *J. Comput. Chem.* **1982**, *3*, 317.

[14] (a) Curtiss, L. A.; Raghavachari, K.; Pople, J. A. *J. Chem. Phys.* **1993**, *98*, 1293. (b) Curtiss, L. A.; Raghavachari, K.; Trucks, G. W.; Pople, J. A. *J. Chem. Phys.* **1991**, *94*, 7221.

[15] (a) 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. For electron affinity data, see: (b) Jordan, K. D.; Burrow, P. D. *Chem. Rev.* **1987**, *87*, 557 and references therein. For the radical addition barrier, see: (c) Kerr, J. A. In *Free Radicals*; Kochi, J., Ed.; Wiley: New York, 1972; Vol. 1.

[16] Wong, M. W.; Pross, A.; Radom, L. *Isr. J. Chem.*, in press.

[17] We use the Mulliken DA (donor–acceptor) terminology. D^3A^* signifies excitation of the alkene to its lowest triplet state.

[18] The G2(MP2) vertical triplet excitation energy of ethylene is 434 kJ mol^{-1} (4.50 eV) (experimental[19] 4.3 eV), and substituents tend to reduce this value (e.g., the calculated value for cyanoethylene is 374 kJ mol^{-1} (3.88 eV)).

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Table I. Calculated Barriers, Enthalpies, Charge Transfers (CT), Ionization Energies (*I*), Electron Affinities (*A*), and Energies of Charge-Transfer States (D^+A^-, D^-A^+) Related to Methyl Addition Reactions to $CH_2{=}CHX$

				I[c]		*A*[c]			
X	barrier[a]	enthalpy[a]	CT[b]	G2(MP2)[d,e]	expt[f]	G2(MP2)[d,e]	expt[f]	D^+A^-[g]	D^-A^+[f]
F	35.7	-93.0	-0.012	10.37	10.36	-1.62	-1.91	11.39	10.33
H	35.2[h]	-92.3[h]	-0.017	10.58	10.51	-1.86	-1.74	11.63	10.54
OH	34.7	-92.1	-0.029	9.26	9.14	-1.75		11.52	9.22
CH_3	33.3	-92.4	-0.024	9.82	9.73	-1.82	-1.95	11.59	9.78
NH_2	31.7	-99.5	-0.039	8.18	(8.20)	-1.92		11.69	8.14
SiH_3	29.8	-101.1	-0.009	10.15	10.1	-0.92		10.69	10.13
Cl	28.5	-105.0	0.000	9.98	9.99		-1.28	11.05[i]	9.94
CHO	24.1	-119.6	0.006	10.21	10.10	0.03		9.74	10.17
NO_2	22.0	-120.4	0.030	11.87		0.79		8.98	11.83
CN	20.4	-127.7	0.012	10.98	10.91	-0.23	-0.21	10.00	10.94

[a] QCISD(T)/6-311G**+ZPVE values,[12] in kJ mol^{-1}. [b] Amount of charge transfer (CT)[13] from the methyl radical to the alkene in the transition structure (HF/6-31G*). A positive value indicates electron transfer from the radical to the alkene. [c] Ionization energies (*I*) and electron affinities (*A*) of alkenes, in eV. [d] G2(MP2) (experimental in parentheses) values for $CH_3^\bullet$ are 9.77 (9.84) (*I*) and 0.04 (0.08) (*A*) eV. [e] Adiabatic values. [f] From ref 15. *I* values are adiabatic, and *A* values are vertical. [g] Charge-transfer energies of separated reactants, calculated from theoretical *I* and *A* values for $CH_3^\bullet$ and $CH_2{=}CHX$. [h] Experimental values (corrected to 0 K) are 38.2 (barrier) and -94.7 (enthalpy) kJ mol^{-1} (from ref 15). [i] Calculated with use of experimental electron affinity for chloroethylene.

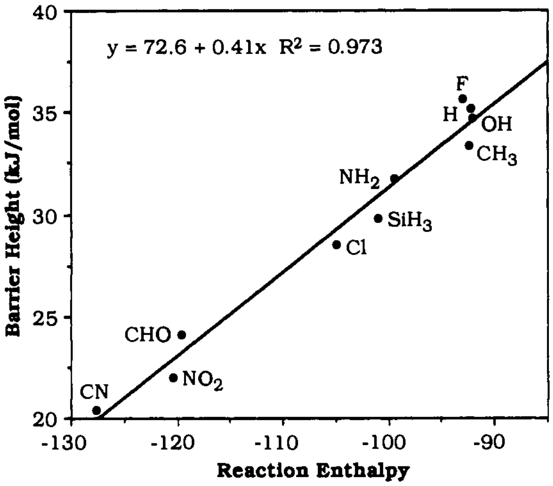

Figure 1. Plot of barrier height against reaction enthalpy for the addition of the methyl radical to alkenes ($CH_2{=}CHX$, X = H, CH_3, NH_2, OH, F, SiH_3, Cl, CN, CHO, and NO_2) (QCISD(T)/6-311G** + ZPVE, kJ mol^{-1}) (see text).

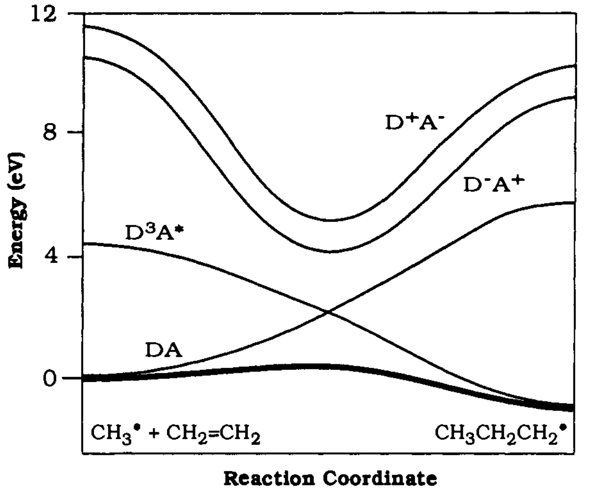

Figure 2. Curve-crossing diagram showing the mixing of DA, D^3A^*, D^+A^-, and D^-A^+ configurations in the schematic generation of the ground-state reaction surface (bold line) for the addition of the methyl radical to ethylene.

ionization energies and electron affinities, listed in Table 1, place the initial energies of D^+A^- and D^-A^+ high and in the range 770–1150 kJ mol^{-1} (8–12 eV). Vertical values for *I* and *A* would increase these values further. However, due to the electrostatic attraction between positive and negative moieties, the energies of the charge-transfer configurations drop sharply as the reactants approach one another. Nonetheless, in the case of methyl radical plus ethylene, the lower energy D^-A^+ configuration is still substantially higher in energy than the crossing point of DA and D^3A^*, probably by approximately 2–3 eV. This large energy separation appears to preclude significant mixing of either D^+A^- or D^-A^+ into the ground-state wave function, consistent with the charge analysis.

In summary, we find that polar contributions to the transition states are small and that reaction exothermicity is the main factor that dominates reactivity. We find no evidence for the prevalent view that the methyl radical is generally nucleophilic toward alkenes.

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(19) Flicker, W. M.; Mosher, O. A.; Kupperman, A. *Chem. Phys. Lett.* **1975**, *36*, 56.