Finally, the results reported in this contribution clearly indicate that differences in resonance energies determine the differences in reactivities of benzenoid hydrocarbons and that the hydrogen isotope exchange reactions follow the simple pathway expressed by eq 1 rather than the more complex pathway proposed by Gold and Satchell.[15]

Conclusion

Logarithms of the rates of deuterodeprotonation of nine alternant hydrocarbons and protodedeuteration of five hydrocarbons containing 17 and 12 different reaction sites, respectively, are correlated with the logarithms of the structure counts of the intermediate, ln SC_I, and the reactant, ln SC_R, and with their ratio, ln (SC_I/SC_R). The quality of the correlations is very good. The results indicate that the differences in reactivities of benzenoid hydrocarbons in aromatic substitution reactions are due to differences in their resonance energies and that hyperconjugation does not play a significant role in the stabilization of the intermediates in the reaction studied.

It is interesting to note that the correlations of the rate data with the calculations based on the structure-resonance theory are much better than those obtained with the HMO localization energies, although both approaches are highly empirical. This is a situation similar to that presented in another recent paper.[16] However, no detailed theoretical explanation for this difference in the quality of the respective correlations can be offered at the present time.

Acknowledgment. Financial support of this work by the Robert A. Welch Foundation, Houston, TX, is gratefully acknowledged. A.S.S. thanks the Robert A. Welch Foundation for a postdoctoral fellowship.

Registry No. 1, 1120-89-4; 2, 875-62-7; 3, 2430-34-4; 4, 14056-37-2; 5, 80160-90-3; 6, 4485-03-4; 7, 4819-99-2; 8, 4819-96-9; 9, 4819-98-1; 10, 80160-91-4; 11, 64615-22-1; 12, 80160-92-5; 13, 80160-93-6; 14, 80160-94-7; 15, 80160-95-8; 16, 80160-96-9; 17, 80160-97-0; benzene, 71-43-2; naphthalene, 91-20-3; anthracene, 120-12-7; phenanthrene, 85-01-8; biphenyl, 92-52-4; pyrene, 129-00-0; benz[a]anthracene, 56-55-3; perylene, 198-55-0; triphenylene, 217-59-4; chrysene, 218-01-9.

---

[15] V. Gold and D. P. N. Satchell, *J. Chem. Soc.*, 3609, 3619, 3622 (1955).

[16] B. A. Hess, Jr., L. J. Schaad, W. C. Herndon, D. Biermann, and W. Schmidt, *Tetrahedron*, 37, 2983 (1981).

On the Thermodynamic Stability and Reactivity of Alkyl-Substituted Alkenes

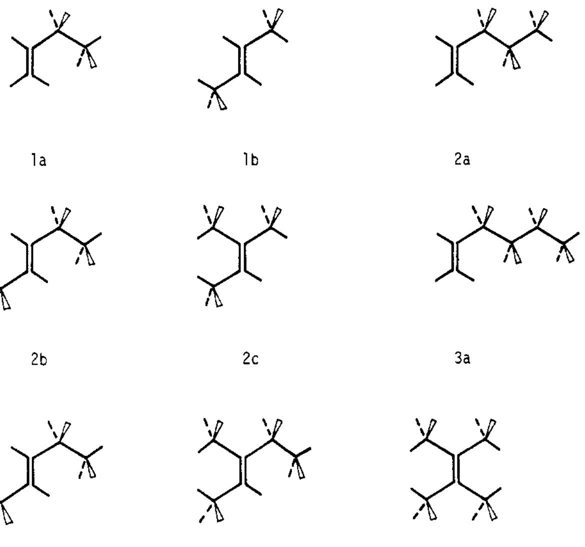
M.-H. Whangbo*† and K. R. Stewart

Department of Chemistry, North Carolina State University, Raleigh, North Carolina 27650

Received September 15, 1981

From heats of formation and heats of hydrogenation data,[1,2] it is observed that the thermodynamic stability of an alkene increases with alkyl substitution. In the hyperconjugation rationale,[3] alkyl group conjugation with a double bond is considered as stabilizing in nature so that an alkene with more alkyl substituents is predicted to be more stable. An alternative rationale focuses upon the C–C and C–H bond energies.[4] Provided that the sum of the C_{sp^3}–C_{sp^2} and C_{sp^3}–H bond energies exceeds that of the C_{sp^3}–C_{sp^3} and C_{sp^2}–H bond energies, the stability of an alkene is expected to increase with alkyl substitution. Those explanations are primarily concerned with the thermodynamic stability of an alkene and do not deal with the change in the reactivity of a double bond induced by alkyl substituents.[5-7]

Chart I



Alkyl substitution is known to greatly enhance the susceptibility of a double bond toward electrophilic attack[5-7] and also to lower the ionization potential of double bond π electrons.[8] From the viewpoint of molecular orbital theory, those results are brought about because alkyl substitution raises the alkene HOMO level.[9] That is, the π-electrons of a double bond become less tightly bound upon alkyl substitution and hence act as a destabilizing factor for the overall thermodynamic stability of the alkene.

Thus, the enhancement of the alkene thermodynamic stability and the raising of the alkene HOMO level are two important aspects to reckon with in any satisfactory explanation of the alkyl substitution effect in alkenes. This effect is an example which counters the empirical observation[10,11] that the HOMO of a molecule parallels the total energy during the course of a molecular conformational change. This observation implies that the most stable isomer of a given molecule would be the one with the lowest-lying HOMO. In order to investigate the alkyl substitution effect in some detail, we have performed ab

---

† Camille and Henry Dreyfus Teacher-Scholar, 1980–1985.

[1] (a) D. R. Stull, E. F. Westrum, Jr., and G. C. Sinke, "The Chemical Thermodynamics of Organic Compounds", Wiley, New York, 1969; (b) C. K. Ingold, "Structure and Mechanism in Organic Chemistry", Cornell University Press, Ithaca, NY, 1953, pp 108–119.

[2] (a) A. Liberles, "Introduction to Theoretical Organic Chemistry", MacMillan, New York, 1968, pp 214–216; (b) M. J. S. Dewar and H. N. Schmeising, ref 3b, pp 83–95.

[3] (a) M. J. S. Dewar, "Hyperconjugation", Ronald Press, New York, 1962, and references therein. (b) V. J. Shiner, Jr., and E. Campaigne, Eds., "Conference on Hyperconjugation", Pergamon Press, New York, 1959.

[4] (a) S. W. Benson and M. Luria, *J. Am. Chem. Soc.*, 97, 3337 (1975); (b) M. J. S. Dewar, ref 3, pp 61–70.

[5] G. H. Schmid and D. G. Garratt, "The Chemistry of Double-Bonded Functional Groups", S. Patai, Ed., Wiley, New York, 1977, Part 2, Chapter 9, and references cited therein.

[6] M. L. Poutsma, *J. Am. Chem. Soc.*, 87, 4285 (1965).

[7] J. E. Dubois and G. Mouvier, *Bull. Soc. Chim. Fr.*, 1426 (1968).

[8] D. A. Demeo and M. A. El-Sayed, *J. Chem. Phys.*, 52, 2622 (1970).

[9] N. D. Epiotis and S. Shaik, *J. Am. Chem. Soc.*, 100, 29 (1978).

[10] M.-H Whangbo and S. Wolfe, *Isr. J. Chem.*, 20, 36 (1980), and references cited therein.

[11] B. M. Deb, *J. Am. Chem. Soc.*, 96, 2030, 2040 (1974).

0022-3263/82/1947-0736$01.25/0

Table I. Energies, HOMO Levels, π-Type Interactions and Total π-Type Interaction Energies for Various Isomers of Alkenes 1-3 [a]

molecule	rel energy, [b] kcal/mol	$-e_{\mathrm{HOMO}}$, eV	interactions [c]	ΔE^{π}, [d] kcal/mol
1a	6.6 (2.7)	8.50	A + B	23.3 (5.2)
1b	0.0 (0.0)	8.08	2A	18.1 (0.0)
2a	6.2 (5.2)	8.48	A + 2B	37.8 (9.9)
2b	2.2 (2.6)	8.06	2A + B	32.5 (4.6)
2c	0.0 (0.0)	7.79	3A	27.9 (0.0)
3a	5.4 (4.2)	8.46	A + 3B	52.5 (14.5)
3b	4.1 (4.1)	8.04	2A + 2B	47.1 (9.1)
3c	2.1 (3.1)	7.77	3A + B	42.3 (4.3)
3d	0.0 (0.0)	7.50	4A	38.0 (0.0)

[a] The geometrical parameters employed in the present work were taken from the study of Epiotis et al.:[18] $r(C_{sp^2}-C_{sp^2}) = 1.3164$ Å, $r(C_{sp^2}-C_{sp^3}) = 1.5313$ Å, $r(C_{sp^3}-C_{sp^3}) = 1.5452$ Å, and $C_{sp^3}-C_{sp^2}-C_{sp^2} = 115°$. All other geometrical parameters are the standard values.[19] The calculated total energies are as follows: $E(\mathbf{1a}) = -154.2348$, $E(\mathbf{1b}) = -154.2453$, $E(\mathbf{2a}) = -192.8142$, $E(\mathbf{2b}) = -192.8206$, $E(\mathbf{2c}) = -192.8241$, $E(\mathbf{3a}) = -231.3938$, $E(\mathbf{3b}) = -231.3958$, $E(\mathbf{3c}) = -231.3991$, and $E(\mathbf{3d}) = -231.4024$ au. [b] The relative energy is given with respect to the most stable structure in each isomeric series of alkenes. The numbers in parentheses refer to the relative energies estimated from the heats of formation data. [c] The symbols A and B refer to type A and type B interactions, respectively. [d] The number in parentheses refers to the relative energy with respect to the most stable structure in each isomeric series of alkenes.

initio SCF MO calculations[12] on alkenes with four to six carbon atoms (see **1**-**3** in Chart I) by employing the STO-3G basis set.[13] The results of these calculations were also analyzed by using the quantitative perturbational molecular orbital (PMO) method,[10,14,15] which enables the evaluation of orbital interaction energies within the framework of the SCF MO theory.

Results and Discussion

Chart I shows the various isomers of the alkenes with four to six carbon atoms. In general, an alkene with two substituents may adopt the *trans*-1,2-, *cis*-1,2-, or 1,1-disubstituted ethylene structure. Since the relative stability of such isomers has already been examined,[10,16] only the *trans*-1,2-dialkylethylene structure was considered for the alkenes with two alkyl groups in the present study. The relative energies and the HOMO levels for the various isomers of **1**-**3**, are listed in Table I. For each isomeric series of the alkenes **1**, **2**, or **3**, both the thermodynamic stability and the HOMO level raising are found to increase with alkyl substitution. Furthermore, the HOMO level raising depends primarily upon the number of alkyl substituents, regardless of the nature of alkyl groups.

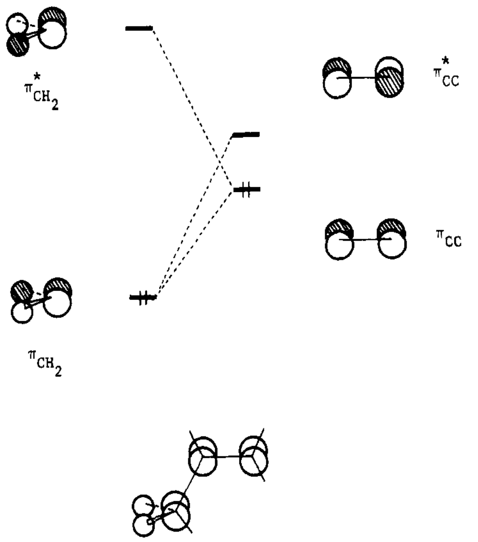


Figure 1. Schematic representation of the π-type orbitals of the double bond and the methylene units in propylene. The stabilizing and destablizing interactions between these orbitals are indicated by the dashed lines. According to the PMO analysis of propylene based upon the STO-3G basis set,[14] the energies of the orbital interactions ($\pi_{CC}-\pi_{CH_2}$), ($\pi_{CH_2}-\pi^*_{CC}$), and ($\pi_{CC}-\pi^*_{CH_2}$) are 14.44, -2.68, and -1.68 kcal/mol, respectively, so that the net result of conjugation between the double bond and the methylene units is destabilizing by 9.78 kcal/mol.

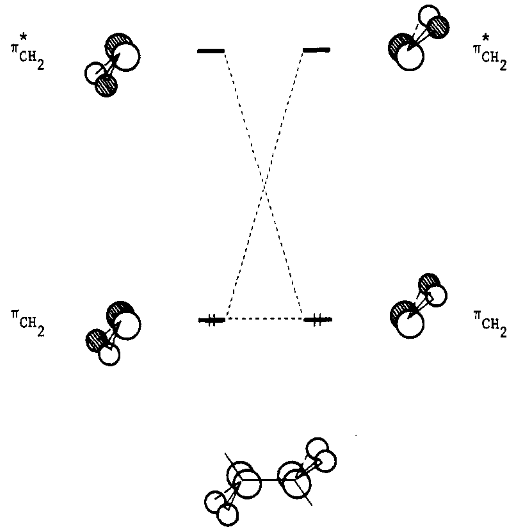


Figure 2. Schematic representation of the π-type orbitals of the two methylene units in ethane. The stabilizing and destabilizing interactions between these orbitals are indicated by the dashed lines. According to the PMO analysis of ethane based upon the STO-3G basis set,[14] the energies of the orbital interactions ($\pi_{CH_2}-\pi_{CH_2}$) and ($\pi_{CH_2}-\pi^*_{CH_2}$) are 15.70 and -0.96 kcal/mol, respectively, so that the net result of conjugation between the two methylene units is destabilizing by 13.78 kcal/mol.

The raising of the HOMO level may now be examined by reference to the π-type orbitals of the double bond and the methylene units in propylene shown in Figure 1. The π-electron level π_{CC} is raised by π_{CH_2} and lowered by $\pi^*_{CH_2}$, but the raising of π_{CC} dominates since π_{CH_2} overlaps better with π_{CC} than does $\pi^*_{CH_2}$.[14] As far as π-type interactions are concerned, an alkyl group may be regarded as made up of methylene units. It appears that π electrons of a double bond are affected mainly by the methylene unit directly attached to the double bond, since the HOMO level raising is primarily determined by the number of alkyl substituents.

Let us now examine the thermodynamic stability of alkenes in terms of orbital interactions. Upon fragmenting an alkyl group into methylene units, π-type orbital interactions present in an alkene can be grouped into two kinds of nearest-neighbor interactions. One is the inter-

---

(12) Our SCF MO calculations were carried out by using the GAUSSIAN 70 program: W. J. Hehre, W. A. Lathan, R. Ditchfield, M. D. Newton, and J. A. Pople, "GAUSSIAN 70", Quantum Chemistry Program Exchange, Indiana University, Bloomington, IN, Program No. 236.

(13) W. J. Hehre, R. F. Stewart, and J. A. Pople, *J. Chem. Phys.*, **51**, 2657 (1969).

(14) M.-H. Whangbo, H. B. Schlegel, and S. Wolfe, *J. Am. Chem. Soc.*, **99**, 1296 (1977).

(15) M.-H. Whangbo, "Computational Theoretical Organic Chemistry", I. G. Csizmadia and R. Daudel, Eds., Reidel, Boston, 1980, p 233.

(16) M.-H. Whangbo, D. J. Mitchell, and S. Wolfe, *J. Am. Chem. Soc.*, **100**, 3698 (1978), and references therein; S. Wolfe, D. J. Mitchell, and M.-H. Whangbo, *Ibid.*, **100**, 1936 (1978).

action between double bond and methylene units (type A), and the other is that between two methylene units (type B). For instance, **2a** has one type A and two type B interactions, while **2b** has two type A and one type B interactions, as summarized in the fourth column of Table I. According to the PMO analysis of propylene,[14] the sum of all the π-type orbital interaction energies present in type A interaction is positive. Namely, the net result of conjugation between the double bond and the methylene units is not stabilizing but destabilizing. An example of type B interaction is found in ethane, the π-type orbitals of which are shown in Figure 2. The PMO analysis of ethane[14] shows that the net result of all the π-type orbital interactions present in type B interaction is destabilizing as well. In addition, type B interaction is found to be more destabilizing than type A interaction due essentially to the fact that the overlap between two neighboring π_{CH_2} orbitals is greater than that between π_{CH_2} and π_{CC}.[14] As summarized in the fourth column of Table I for each isomeric series of the alkenes **1**, **2**, or **3**, the number of type A interactions increases but that of type B interactions decreases with alkyl substitution. Since type A interaction is less repulsive than type B interaction, the thermodynamic stability of the alkene is expected to increase with alkyl substitution. The π_{CC} orbital of a double bond is raised by type A interaction, so the raising of the alkene HOMO is expected to increase with alkyl substitution as well.

The last column of Table I lists the total π-type orbital interaction energy ΔE^{π} for each alkene. By employing the PMO method,[14,15] this energy was estimated as the orbital energy difference defined in eq 1, where the first summation includes all the occupied π-type orbitals of a given alkene while the second summation includes those of the alkene fragments (i.e., the double bond and methylene units of the alkene).[17] As expected from the above discussion, the interaction energy ΔE^{π} becomes less repulsive as the number of alkyl substituents increases in each isomeric series of the alkenes **1**, **2**, or **3**.

$$\Delta E^{\pi} = 2\sum_{i}^{\mathrm{occ}} e_i^{\pi}(\text{alkene}) - 2\sum_{i}^{\mathrm{occ}} e_i^{\pi}(\text{fragments}) \qquad (1)$$

Concluding Remarks

Alkyl substitution enhances the thermodynamic stability of an alkene and raises the HOMO level of the alkene as well. These two effects are accounted for by noting that the net result of conjugation between double bond and methylene units is destabilizing in nature, as is that between two methylene units, but the former is less destabilizing.

Acknowledgment. This work was supported by the Research Corp. through a Cottrell Research Program, which is gratefully acknowledged. We are thankful to Professors E. M. Arnett, P. v. R. Schleyer, and S. Wolfe for helpful discussions.

Registry No. 1a, 106-98-9; **1b**, 624-64-6; **2a**, 109-67-1; **2b**, 646-04-8; **2c**, 513-35-9; **3a**, 592-41-6; **3b**, 13269-52-8; **3c**, 616-12-6; **3d**, 563-79-1.

---

[17] Within the framework of SCF MO theory, orbital energy variation is caused not only by orbital interaction but also by potential change.[15] In the Fock matrix partitioning method of defining fragment orbitals,[14,15] which was adopted in the present work, the effect of potential change is incorporated into fragment orbital energies.[15] Thus, eq 1 measures the orbital energy change induced by orbital interaction.

[18] N. D. Epiotis, R. L. Yates, and F. Bernardi, *J. Am. Chem. Soc.*, **97**, 5961 (1975).

[19] J. A. Pople and M. Gordon, *J. Am. Chem. Soc.*, **89**, 4253 (1967).

Retro-Diels–Alder, γ-Hydrogen Rearrangement, and Decarboxylation Reactions. Pathways for Fragmentation in the Collision Activated Dissociation Mass Spectra of Ketones and Carboxylic Acid $(M - 1)^-$ Ions

Donald F. Hunt,* Anne B. Giordani, Jeffrey Shabanowitz,
and Gerald Rhodes

*Department of Chemistry, University of Virginia,
Charlottesville, Virginia 22901*

Received July 21, 1981

Fragment ions observed in the collision activated dissociation mass spectra of ketone $(M - 1)^-$ ions can be explained by either a retro-Diels–Alder reaction or a γ-hydrogen (McLafferty) rearrangement.[1] Here we present evidence in support of the postulated mechanisms for these novel fragmentation pathways of negative ions.

Collision activated dissociation mass spectra were obtained on a triple quadrupole mass spectrometer that has been described in detail elsewhere.[1] This instrument employs a chemical-ionization source, three quadrupole mass filters, and a conversion dynode electron multiplier detector.[2]

Negative ion mass spectra were generated under chemical-ionization conditions with either CH_4/N_2O or $MeOH/N_2O$ mixtures as the reagent gas.[3] The anions OH^- and MeO^- are produced as shown in eq 1–3 and were employed as the chemical-ionization reactant ions in the present work. Both of these species function as strong Brønsted bases in the gas phase and abstract protons from the carbon α to the carbonyl group in ketones (eq 4 and 5).[4]

$$N_2O + e^- \rightarrow N_2 + O^{-\cdot} \qquad (1)$$

$$O^{-\cdot} + CH_4 \rightarrow OH^- + CH_3\cdot \qquad (2)$$

$$O^{-\cdot} + MeOH \rightarrow MeO^- + OH\cdot \qquad (3)$$

$$OH^- + CH_3COCH_3 \rightarrow H_2O + CH_3COCH_2^- \qquad \Delta H = -19\ \text{kcal} \quad (4)$$

$$MeO^- + CH_3COCH_3 \rightarrow MeOH + CH_3COCH_2^- \qquad \Delta H = -9\ \text{kcal} \quad (5)$$

Collision activated dissociation mass spectra were obtained by using the first quadrupole mass filter to mass select the parent $(M - 1)^-$ ion and transmit it to the second quadrupole. The chamber containing this latter quadrupole was filled with nitrogen to a pressure of 2–6 mtorr, and the quadrupole was operated with only rf voltage on the rods. In this mode of operation, the quadrupole functions as a highly efficient collision cell and both focuses and transmits ions of all possible m/z values. When the parent $(M - 1)^-$ ion enters the second quadrupole, it suffers

---

[1] Hunt, D. F.; Shabanowitz, J.; Giordani, A. B. *Anal. Chem.* **1980**, *52*, 386–390.

[2] Stafford, G. C.; Reeher, J.; Smith, R.; Story, M. *Dyn. Mass Spectrom.* **1978**, *5*, 55–57.

[3] Smit, A. L. C.; Field, F. H. *J. Am. Chem. Soc.* **1977**, *99*, 6471–6483.

[4] Enthalpy changes for the reaction channels discussed in this paper are estimated from heats of formation and proton affinity data that are either taken from ref 4a,b or estimated by the group equivalent method of ref 4c: (a) Rosenstock, H. M.; Draxl, K.; Steiner, B. W.; Herron, J. T. *J. Phys. Chem Ref. Data, Suppl. 1* **1977**, *6*, 774–783. (b) Bartmess, J. E.; McIver, R. T. "Gas Phase Ion Chemistry"; Bowers, M. T., Ed.; Academic Press: New York, 1979; Chapter 11. (c) Benson, S. W. "Thermochemical Kinetics", 2nd ed.; Wiley-Interscience: New York, 1976.

0022-3263/82/1947-0738$01.25/0