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(18) Camille and Henry Dreyfus Teacher–Scholar Grant Recipient, 1971–1976.

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*Received December 11, 1974*

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## Benzoyl Cations. The Correlation of Thermodynamic Stabilities and $^{13}C$ Nuclear Magnetic Resonance Chemical Shifts with Hammett σ Values and CNDO/2 Charge Densities

*Sir:*

Recently there has arisen a controversy over the extent to which $^{13}C$ chemical shifts can be used as a measure of the charge distribution in stable carbocations in superacid media.[1,2] Due to the extensive use of $^{13}C$ chemical shifts as an indication of charge distribution in carbocations, this is an important issue. We have measured relative thermodynamic stabilities and carried out CNDO/2 calculations on a series of substituted benzoyl cations for which $^{13}C$ NMR chemical shifts are available.[3,4] While the thermodynamic stabilities correlate nicely with Hammett σ values, the $^{13}C$ chemical shifts do not. The acyl carbon $^{13}C$ chemical shift shows a rather scattered but obvious linear correlation with the CNDO/2 charge density. Correlations having a ***negative*** slope are observed between calculated charge densities and $^{13}C$ chemical shifts of the ring carbons.

The relative heats of formation ($\Delta H_{R+}$) of a series of benzoyl cations in 11.5 mol % antimony pentafluoride–fluorosulfonic acid at 25° are plotted vs. σ in Figure 1. The relative heats of formation are, as before,[5-7] heats of transfer of the precursor from dilute solution in carbon tetrachloride to dilute solution in the superacid and give accurate values for the substituent effect on the enthalpy required to convert the covalent precursor into the cation. All ions are quite stable and are formed cleanly, as verified by NMR work both in our laboratories and others.[3] The excellent straight line obtained when $\Delta H_{R+}$ is plotted against σ indicates that the normal Hammett σ values are quite appropriate for use in the superacid medium. There are no unusual solvent effects occurring which would make necessary the use of another set of substituent parameters. A correlation with σ rather than $\sigma^+$ is expected since, in both the ground state molecule and the ions, the substituents and the reaction center are directly conjugated.[8] The relative heats of formation reported here also give a good correlation with the solvolysis rates for some of the same benzoyl chlorides in aqueous formic acid.[9] When the $^{13}C$ chemical shifts are plotted vs. σ, no correlation is observed. A very general trend is observed when $\sigma^+$ is used, but the correlation is still very poor. This absence of a correlation of δ $^{13}C$ with σ contrasts with previously observed correlations of δ $^{13}C$ with σ in di- and triphenyl methyl cations.[10,11]

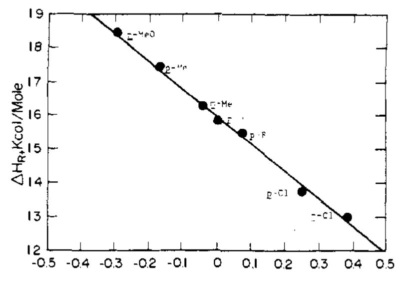


**Figure 1.**

Table I contains the $^{13}C$ chemical shifts together with charge densities calculated using Pople's CNDO/2 technique.[12] Standard geometries were used and the charge densities calculated using the standard and X-ray geometries for the *p*-methylbenzoylium ion were quite similar, as shown.[13] The ring-$C_\alpha$ bond length used was 1.387 Å and the -C=O bond length adopted was 1.111 Å, based on X-ray data.[14] The C-Cl bond length used was 1.70 Å. In row 9 of the table, the equation for the least-squares plot of charge density vs. δ $^{13}C$ is reported. The acyl carbon shows a linear plot, correlation coefficient 0.908, with a slope of 629 ppm/electron. This is a much greater slope than that usually reported, ca. 160 ppm/electron.[15,16] Furthermore, the ring carbons all give negative slopes when σ is plotted against the charge density. Thus different carbon atoms in the same molecule give different slopes when their δ $^{13}C$ is plotted vs. charge density. The problem does not seem to lie in the geometry used for the CNDO/2 calculations. As shown in Table I and as expected for the parameterization of the CNDO/2 method, the calculated charge densities are not very sensitive to small changes in geometry. The results for the *p*-methylbenzoylium ion are quite similar using the X-ray geometry, which shows significant ring distortion, and Pople's standard geometry. However, it is quite possible that these calculations are not giving accurate charge densi-

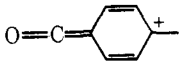
Table I. Carbon-13 Chemical Shifts,[a] Calculated Charge Densities,[b] and Their Least-Squares Correlation in Substituted Benzoyl Cations

| X | $C_\alpha$ |  | $C_1$ |  | $C_2$ |  | $C_3$ |  | $C_4$ |  | Other shifts and charge densities |
|---|---|---|---|---|---|---|---|---|---|---|---|
|  | δ | Charge | δ | Charge | δ | Charge | δ | Charge | δ | Charge |  |
| H | 38.9 | 0.5004 | 106.0 | −0.0330 | 52.4 | 0.0881 | 60.8 | 0.0063 | 44.3 | 0.0876 |  |
| *p*-$CH_3$ (std) | 37.2 | 0.4891 | 110.9 | −0.0525 | 53.4 | 0.0912 | 60.2 | −0.0170 | 27.4 | 0.1339 | $CH_3$, 169.2, −0.0407 |
| *p*-$CH_3$ (X-ray) |  | 0.4797 |  | −0.0628 |  | 0.0922 |  | −0.0261 |  | 0.1551 | $CH_3$, −0.0769 |
| *p*-F | 39.1 | 0.4990 | 110.3 | −0.0494 | 48.3 | 0.1069 | 71.8 | −0.0496 | 18.0 | 0.3208 |  |
| *p*-Cl | 37.6 | 0.4991 | 106.6 | −0.0324 | 47.8 | 0.0884 | 55.7 | 0.0093 | 32.8 | 0.1432 |  |
| *p*-$CH_3O$– | 32.3 | 0.4917 | 116.6 | −0.0608 | 48.9 | 0.1060[c] | 73.5 | −0.0685[d] | 17.3 | 0.2703 | $CH_3O$, 133.9, −0.1731 |
| *m*-$CH_3$– | 37.0 | 0.4929 | 105.4 | −0.0325 | 52.5 | 0.0590 | 47.8 | −0.0556 | 41.7 | 0.0655 | $C_5$, 60.8, 0.0131<br>$C_6$, 53.5, 0.0735 |
| *p*-C=$O^+$ | 48.5 | 0.5150 | 85.3 | 0.0351 | 52.1 | 0.0815 |  |  |  |  |  |
| Correlation line, CD = | 0.00159δ + 0.437 |  | −0.00320δ + 0.307 |  | −0.00402δ + 0.293 |  | −0.00448δ + 0.266 |  | −0.00827δ + 0.420 |  |  |
| Correlation coefficient | 0.908 |  | 0.994 |  | 0.580 |  | 0.976 |  | 0.928 |  |  |

[a] Measured in $SbF_5$ at 20°, in ppm from $^{13}CS_2$ ($\delta_{TMS}{}^{CS_2}$ 193.7), from ref 3. [b] CNDO/2, standard bond lengths and angles used. [c] Average of syn and anti (to O–$CH_3$). [d] Syn to O–$CH_3$, anti −0.0534.

ties for the ions involved. More sophisticated calculations might shed light in this question.

An examination of the data in Table I reveals that the chemical shifts for the ring carbons often move in a direction opposite to that expected on substituent changes. For example, replacing a H in benzene by a methyl group causes a shift of −3.1 ppm in the para position while the para-carbon (*i.e.*, $C_1$) shifts by +4.9 when the same substitution is made in the benzoylium ion. This behavior was rationalized[3] as being due to the large contribution of a "ketene like" resonance form (**1**). Such forms are known to be important from X-ray data.[13,14] However, ketene-like structures cannot explain the negative slope of the $\delta$ $^{13}C$ is charge density plot for *all* the ring carbons.



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These results show that one cannot always expect to find a correlation between $^{13}C$ chemical shifts and $\sigma$. Also, while correlations of CNDO/2 charge densities with $\delta$ $^{13}C$ exist for neutral molecules and the theory seems to be well developed, the same is not true for charged systems. The occurrence of opposite correlation slopes within the same molecule points out dramatically the need for both more elegant calculations and more experimental work to elucidate fully the correlation between $\delta$ $^{13}C$ and charge densities in *charged systems*. Whether the fault lies with the calculations on charged molecules or at more basic levels, we are forced to the conclusion that correlations of $^{13}C$ chemical shifts with calculated charge densities in carbocations are not yet well understood and may fail. While we are not willing to generalize on the basis of this one system and universally condemn the use of $^{13}C$ NMR chemical shifts as an index of charge density, these results do make it clear that caution must be used in obtaining charge distributions from $^{13}C$ chemical shifts. More work should be done on simple cationic systems attempting to correlate $^{13}C$ NMR chemical shifts with various indicators of charge density in order to examine the general validity of the suggested relationship between charge density and chemical shift, and, if the relationship is valid, to calibrate it. These data also illustrate the danger of assuming correlations between electron distribution (or $\delta$ $^{13}C$) and thermodynamic stability.[17]

**Acknowledgment.** Support of this work by the National Science Foundation is gratefully acknowledged, as are the comments of Professor Olah. We are grateful for the advice and aid of Professor John Bloor in carrying out the CNDO/2 calculations.

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## Thermodynamic Limitations in Chemiluminescent Reactions

*Sir:*

Despite the current interest in chemiluminescence, there is no clear understanding as to why some reactions are chemiluminescent and others are not. For example, thermolysis of 1,2-dioxetanes[1] leads to an excited-state ketone with a quantum yield approaching 1. In contrast, thermolysis of Dewar benzenes[2] leads to triplet-state benzene, but with a quantum yield of only 0.02–0.1%. These reactions seem quite similar, in that both lead from strained reactants to very stable products, with an exothermicity close to the energy of a visible photon. McCapra[3] and Kearns[4] have suggested that dioxetanes should be chemiluminescent because a ground-state orbital correlates with an excited orbital of the product ketones. Turro and Lechtken[5] have attributed the high chemiluminescent efficiency in thermolysis of dioxetanes to vibronic coupling during a concerted cleavage. Richardson et al.[6] have attributed the high yield to a rapid intersystem crossing of a biradical intermediate. Dewar[7] has suggested that high chemiluminescent efficiency requires a transition state with the highest occupied and lowest vacant molecular orbitals nearly degenerate. Yet there are also thermodynamic limitations on chemiluminescent yields, and a consideration of these limitations clarifies the contrast between dioxetanes and Dewar benzenes.

How can a reaction that is exothermic by only 60–71 kcal/mol[2,8] produce an excited state 78–85 kcal/mol[9] above the ground state? Obviously, the first law of thermodynamics must not be violated, and, in recognition of the first law, the accepted resolution of this apparent violation is that the energy difference comes from the activation energy, which is 22–28 kcal/mol[2,10] (Figure 1a). By such reasoning, reactions with an extremely high activation energy should be capable of converting thermal energy into light. For example, isomerization of norbornadiene should produce excited-state toluene, since the reaction[11a] is exother-

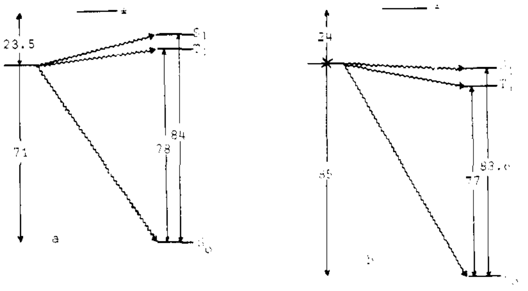

**Figure 1.** Energetics of reactant, transition state, and possible products in dioxetane thermolysis, which can produce excited singlet ($S_1$) and triplet ($T_1$) states: (a) enthalpy, in kcal/mol; (b) free energy, in kcal/mol, at 25°.