

pathway for carbon–carbon bond scission on (1×1)Pt(110).

In contrast, however, on (2×1)Pt(110) the methyl group in an upright ethylidyne would overlap both the C₇ and the C₉ atom on the (2×1)Pt(110) surface as shown in Figure 5C. While the overlap with the C₉ atom decreases as the bond extends, the overlap with C₇ atom increases. The increase in the overlap with the C₇ is larger than the decrease in the overlap with the C₉ atom. Consequently, while there is a driving force for bond extension on (1×1)Pt(110), the extra steric hindrances on the (2×1)Pt(110) surface would inhibit carbon–carbon bond scission on (2×1)Pt(110). As a result, the mechanism in Figure 4B explains why bond scission is more likely on (1×1)Pt(110) than on (2×1)Pt(110) as is observed.

If bond scission occurs, one would produce a methyl group. Henderson et al.¹⁵ show that methane formation from recombination of hydrogen and methyl radicals occurs quite readily at 290 K on Pt(111) in the presence of chlorine. Hence, similar chemistry is quite feasible on (1×1)Pt(110).

Admittedly, the mechanism in Figure 4B is speculative. We do not have direct evidence that a deformed ethylidyne actually forms on (1×1)Pt(110). There is a 1350-cm⁻¹ stretch in EELS which might be associated with either a deformed ethylidyne or some other species containing a CH₃ group such as an isolated methyl group. However, our evidence for formation of a strained ethylidyne intermediate is not strong. Still, the mechanism in

Figure 4B does explain our observations. All of the steps except the carbon–carbon bond scission step have been observed previously on other faces of platinum. A carbon–carbon bond scission process clearly occurs since we observe a methane desorption product. We observe a decrease in the methane desorption temperature as we add surface hydrogen, which is suggestive that the methane forms via a recombination process. However, isotopic exchange experiments to prove this mechanism were inconclusive. Thus, we propose the mechanism in Figure 4B as a tentative, but by no means definitive, explanation of our data.

Conclusions

In summary then, in this paper we present the first clear evidence for methane formation during ethylene decomposition on any single-crystal transition-metal surface. We find that methane formation occurs on a (1×1) reconstruction of Pt(110). However, it is not observed on the (2×1) reconstruction of Pt(110). Yet there are no sites present on (1×1)Pt(110) which are not also present on (2×1)Pt(110). We have proposed that the methane formation occurs by the mechanism in Figure 4B. All of the steps in this mechanism have been observed on other surfaces of platinum. Further, the mechanism in Figure 4B explains our observations, including the unprecedented structure sensitivity of the methane formation reaction. However, our evidence for this mechanism is by no means definitive.

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(15) Henderson, M. A.; Mitchell, G. E.; White, J. M. *Surf. Sci. Lett.* **1987**, *184*, L325.

(16) Kesmodel, L. L.; Dubois, L. H.; Somorjai, G. A. *Chem. Phys. Lett.* **1978**, *56*, 267.

(17) Skinner, P.; Howard, M. W.; Oxtou, I. A.; Kettle, S. F. A.; Powell, D. B.; Sheppard, N. *J. Chem. Soc., Faraday Trans. 2* **1981**, *77*, 1203.

(18) Adams, D. L.; Nielsen, H. B.; VanHove, M. A.; Ignatiev, S. *Surf. Sci.* **1987**, *104*, 47.

Determination of the Acidity of Lewis Acids

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Abstract: The chemical shift (H-3) of crotonaldehyde complexed by a Lewis acid provides a measure of its strength as a catalyst, according to R. F. Childs, D. L. Mulholland, and A. Nixon, (*Can. J. Chem.* **1982**, *60*, 801–808). A theoretical justification was highly desirable and is provided here: the experimental method works because of the linear dependence of the H-3 chemical shift on the energy of the lowest π^* MO in the complex. While the experimental determination has some drawbacks (problems of precise concentration, solubility, impurities, and availability), MO calculations appear trustworthy and have some advantages for the estimation of the catalytic activity of a Lewis acid.

Introduction

Numerous recent studies make use of Lewis acids to catalyze organic reactions. These include, as prime examples, Diels–Alder¹ and [2 + 2]² cycloadditions, ene reactions,³ aldol condensations,^{1e–4}

Michael 1,4-additions,⁵ the reaction of acetals with olefins and unsaturated ethers,⁶ and Claisen⁷ rearrangements, besides other textbook cases such as Friedel–Crafts alkylations and acylations.⁸

(1) (a) Lamy-Schelkens, H.; Gioni, D.; Ghosez, L. *Tetrahedron Lett.* **1989**, *30*, 5887–5890. (b) Maruoka, K.; Yamamoto, H. *J. Am. Chem. Soc.* **1989**, *111*, 789–790. (c) Midland, M. M.; Afonso, M. M. *J. Am. Chem. Soc.* **1989**, *111*, 4368–4371. (d) Narasaka, K.; Iwasawa, N.; Inoue, M.; Yamada, T.; Nakashima, N.; Sugimori, J. *J. Am. Chem. Soc.* **1989**, *111*, 5340–5345. (e) Corey, R.; Imwinkelried, E. J.; Pikul, S.; Xiang, Y. B. *J. Am. Chem. Soc.* **1989**, *111*, 5493–5495.

(2) (a) Doxsee, K. M.; Farahi, J. B. *J. Am. Chem. Soc.* **1988**, *110*, 7239–7240. (b) Trost, B. M.; Yany, B.; Miller, M. L. *J. Am. Chem. Soc.* **1989**, *111*, 6482–6484. (c) Lewis, F. D.; Baranyk, S. V. *J. Am. Chem. Soc.* **1989**, *111*, 8653–8661.

(3) (a) Snider, B. B. *Acc. Chem. Res.* **1980**, *13*, 426–432. (b) Tietze, L. F.; Beifuss, U.; Ruther, M. *J. Org. Chem.* **1989**, *54*, 3120–3129. (c) Mikami, K.; Terada, M.; Nakai, T. *J. Am. Chem. Soc.* **1989**, *111*, 1940–1941.

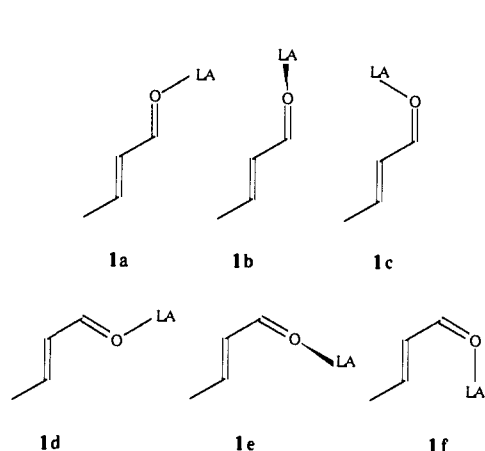
(4) (a) Ojima, I.; Kwon, H. B. *J. Am. Chem. Soc.* **1988**, *110*, 5617–5621. (b) Danishefsky, S. J.; Simoneau, B. *J. Am. Chem. Soc.* **1989**, *111*, 2599–2604. (c) Hegel, G.; Thornton, E. R. *J. Am. Chem. Soc.* **1989**, *111*, 5722–5728.

(5) (a) Lipshutz, B. H.; Ellsworth, E. L.; Siahaan, T. J. *J. Am. Chem. Soc.* **1988**, *110*, 4834–4835. (b) Lipshutz, B. H.; Ellsworth, E. L.; Siahaan, T. J. *J. Am. Chem. Soc.* **1989**, *111*, 1351–1358. (c) Cabral, J.; Laszlo, P.; Mahé, L.; Montaufier, M. T. *Tetrahedron Lett.* **1989**, *30*, 3969–3972.

(6) (a) Povarov, L. S. *Russ. Chem. Rev. (Engl. Transl.)* **1975**, *34*, 639–656. (b) Hoaglin, R. J.; Hirsh, D. H. *J. Am. Chem. Soc.* **1949**, *71*, 3468–3472. (c) Isler, O.; Lindlar, H.; Montavon, M.; Rüegg, R.; Zeller, P. *Helv. Chim. Acta* **1956**, *39*, 249–259. (d) Isler, O.; Montavon, M.; Rüegg, R.; Zeller, P. Swiss Patent 317112, 1956.

(7) (a) Maruoka, K.; Nonoshita, K.; Banno, H.; Yamamoto, H. *J. Am. Chem. Soc.* **1988**, *110*, 7922–7924. (b) Nonoshita, K.; Banno, H.; Maruoka, K.; Yamamoto, H. *J. Am. Chem. Soc.* **1990**, *112*, 316–322.

Chart I



The choice of the appropriate Lewis acid and the amount in which it should be used continue to tax the ingenuity and intuition of the chemist. As a rule, trial and error remains the best way to answer these questions. Accordingly, the study by Childs et al.⁹ of the ¹H NMR spectra of 1:1 complexes of α,β -unsaturated carbonyls and Lewis acids gave extremely useful results. At a site remote from a locus of complexation (an oxygen lone pair), such as position 3 in crotonaldehyde, the chemical shift of the attached proton changes significantly and smoothly with the nature of the Lewis acid. This remained an empirical finding. We launched the present study for two reasons: viz. to give it a more secure theoretical foundation and to try to better understand why NMR measurements fail to predict accurately the chemical activity of Lewis acids as catalysts.¹⁰ We decided to restrict the study, at least in its present format, to α,β -unsaturated carbonyls, molecules such as acrolein, acrylic acid and acrylates, methyl vinyl ketone, and methacrolein. These are important for both synthetic and industrial purposes, as dienophiles (Diels–Alder), as enophiles (ene), as Michael acceptors—to quote three important reactions catalyzed by Lewis acids. Thus, the concept we set out to investigate can be simply stated: *Since, as is well-known, complexation by a Lewis acid lowers all the molecular orbitals in such α,β -unsaturated carbonyls, there ought to be a relationship between the extent of this lowering and, on the one hand, the catalytic activity and, on the other hand, the chemical shift changes attendant upon such complexation.*

Methods

The magnitude of chemical shift variations that can be monitored by the Childs et al. method⁹ (0.6–1.5 ppm) is so large as to lead one to expect very significant changes in the position of the MO levels in the Lewis acid– α,β -unsaturated carbonyl complexes, as well. Accordingly, we elected to make semiempirical calculations at the MNDO level. With such big effects, even relatively unsophisticated treatments should reproduce them. A second reason was our desire to make this approach available very widely. The MNDO program¹¹ is available from the QCPE library and it requires only relatively modest amounts of computer time. Conversely, the MNDO treatment is of sufficient quality, we felt, to make the results trustworthy. The MNDO method is well-suited for accurate calculation of atomic charges. Generally, it gives electronic distributions and dipole moments in good agreement with experimental data.¹¹ Since, as we shall see, the NMR chemical shift serves in the method of Childs et al.⁹ to monitor a charge variation, MNDO calculations should be adequate to this task.

The input is a geometry. We consider the six conformations for complexed crotonaldehyde, **1a–1f**, shown in Chart I (LA stands for Lewis acid). The *s-trans* conformations **1a–1c** correspond to complexation of the Lewis acid on the anti or syn sp^2 lone pair (**1a** and **1c**) or on the 2s lone pair on oxygen (**1b**). Likewise, the *s-anti* conformations **1d–1f** are also considered. A subroutine consisting of the MAD package, i.e., a

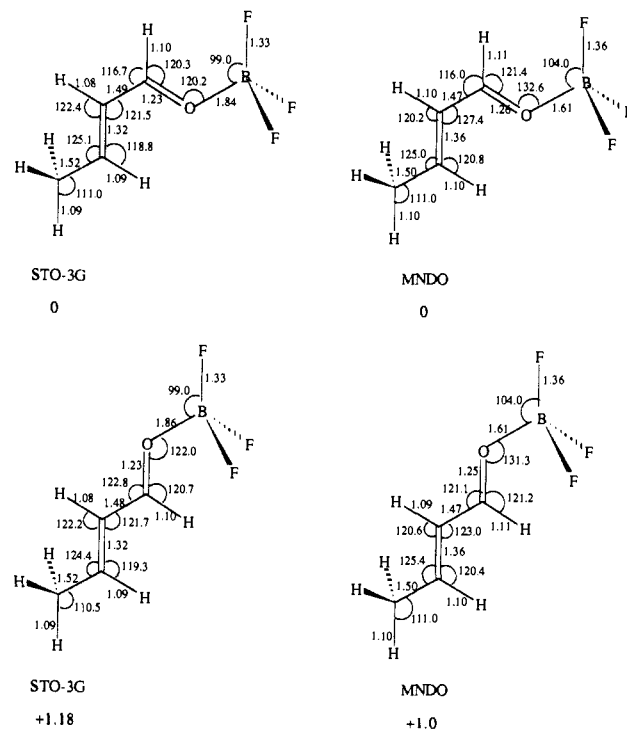
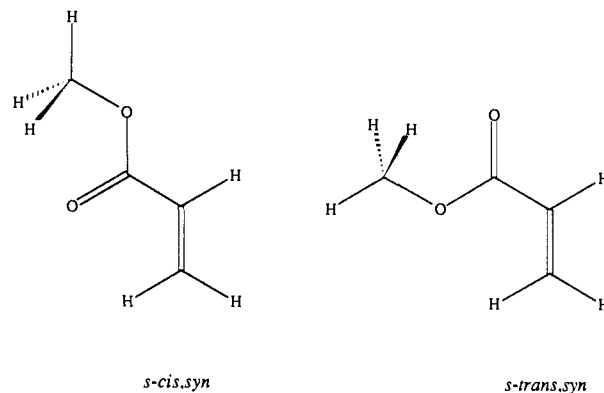


Figure 1. Comparison of calculated geometries and relative energies obtained by ab initio (STO-3G) and by MNDO methods for conformations **1a** and **1d** of crotonaldehyde.

Chart II



molecular mechanics program,¹² is used to generate initial values of the atomic coordinates. The MNDO program is then used for a geometry optimization for each of the subsets **1a–1f**. We checked also that the key geometrical conclusions from MNDO calculations are trustworthy. One such control is provided by the results obtained by the Houk group on Lewis acid complexes of acrolein, acrylic acid, and methyl acrylate.¹³ For this last molecule, the 3-21G ab initio least energy geometry computed by Loncharich et al.¹³ is the *s-cis, syn*, with the *s-trans, syn* 0.8 kcal·mol⁻¹ above it (Chart II). We performed another control by running parallel ab initio STO-3G and MNDO calculations on crotonaldehyde–BF₃ complexes **1a** and **1d** (Figure 1). The ab initio and the semiempirical results converge as to the most stable conformations even though the computed geometries differ in a number of respects.

Results

In all cases studied (Table I), for the crotonaldehyde complexes conformation **1d** was that of lowest energy according to our MNDO calculations. Steric factors influence these conformational preferences. For instance, when an OR group from an ester is present, as with methyl acrylate, the most stable geometry becomes that related to **1c**.

(8) Olah, G. A. *Friedel–Crafts and Related Reactions*; Interscience Publishers: New York, 1964.

(9) Childs, R. F.; Mulholland, D. L.; Nixon, A. *Can. J. Chem.* **1982**, *60*, 801–808.

(10) Bonnesen, P. V.; Puckett, G. L.; Honeychuck, R. V.; Hersh, W. H. *J. Am. Chem. Soc.* **1989**, *111*, 6070–6081.

(11) Dewar, M. J. S.; Thiel, W. *J. Am. Chem. Soc.* **1977**, *99*, 4899–4907.

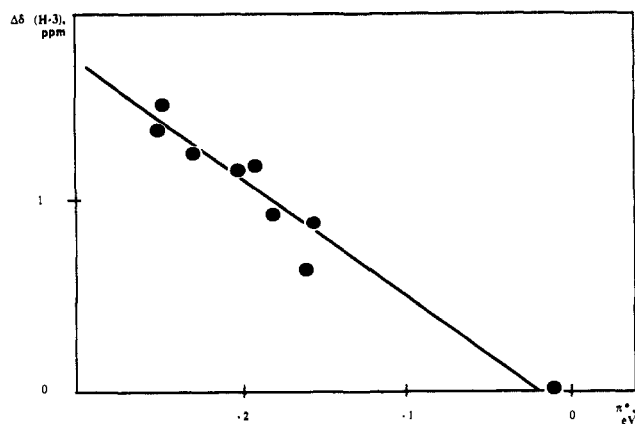
(12) Lahana, R. *Molecular Advanced Design*; Pierre Fabre Médicaments, F-81 Castres, France.

(13) Loncharich, R. J.; Schwartz, T. R.; Houk, K. N. *J. Am. Chem. Soc.* **1987**, *109*, 14–23.

Table I. Sequence of Lewis Acidities Obtained by the MNDO Method and Comparison with Other Methods^a

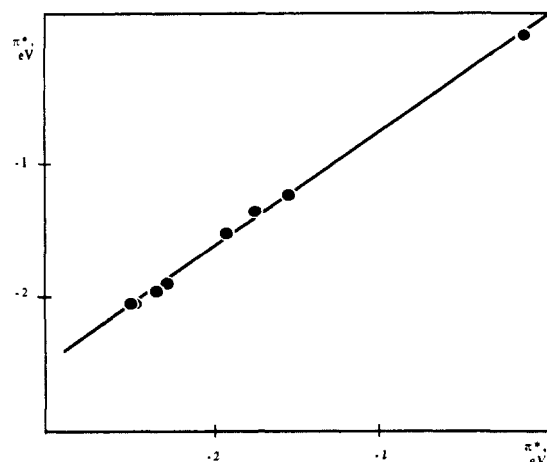
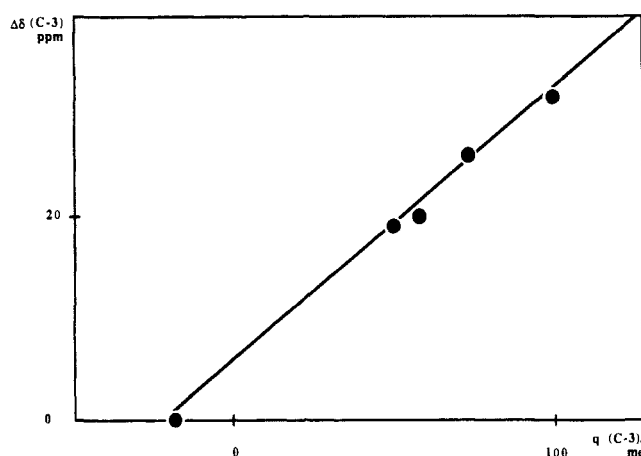
| Lewis acids | MNDO | | | IR ^d $\Delta\nu$, cm ⁻¹ | NMR ^b $\Delta\delta$, ppm |
|-------------------------|--|--------------|-------------------------------------|---|--|
| | ΔH_{int}^c , kcal·mol ⁻¹ | π^* , eV | relative Lewis acidity ^d | | |
| BCl ₃ | -6.63 | -2.52 | 1.00 | 176 | 1.35 |
| BBr ₃ | -8.17 | -2.50 | 0.99 | 191 | 1.49 |
| SiCl ₄ | -0.26 | -2.43 | 0.96 | | |
| AlBr ₃ | -26.28 | -2.37 | 0.94 | 138 | |
| AlCl ₃ | -25.57 | -2.31 | 0.91 | 117 | 1.23 |
| EtAlCl ₂ | -19.97 | -2.03 | 0.80 | | 1.15 |
| BF ₃ | +4.13 | -1.93 | 0.76 | 119 | 1.17 |
| Et ₂ AlCl | -15.56 | -1.82 | 0.71 | | 0.91 |
| AlF ₃ | -16.25 | -1.77 | 0.69 | | |
| Me(OPh) ₂ Al | -11.40 | -1.76 | 0.68 | | |
| HgCl ₂ | -2.49 | -1.74 | 0.68 | | |
| HgBr ₂ | +4.38 | -1.72 | 0.67 | | |
| HgF ₂ | -0.47 | -1.71 | 0.66 | | |
| HgI ₂ | +9.78 | -1.66 | 0.64 | | |
| Et ₃ Al | -10.09 | -1.62 | 0.63 | | 0.63 |
| SnCl ₄ | +10.05 | -1.58 | 0.61 | 128 | 0.87 |
| AlH ₃ | -16.86 | -1.56 | 0.60 | | |
| HgH ₂ | +16.76 | -0.99 | 0.36 | | |

^a Shifts of the carbonyl stretching frequency in ethyl acetate complexes.²⁴
^b Variations of H-3 chemical shift in crotonaldehyde.⁹ ^c Calculated MNDO values for the energies of interaction (heat of formation of the complexes - sum of heats of formation of the reactants). ^d BCl₃ = 1.00 and the π^* energy of uncomplexed crotonaldehyde (-0.11 eV) used to define the zero of the Lewis acidity scale. ^e Comparison with the compilation by Satchell²⁵ is made difficult by the variety of the bases against which Lewis acids are pitted and by solvent effects.

**Figure 2.** Chemical shift variations for the H-3 proton in crotonaldehyde as a function of the energy of the lowest π^* MO in the complex.

A first test is that of the correspondence between these calculated values and the NMR chemical shifts. We plot in Figure 2 the chemical shift for the H-3 proton in the crotonaldehyde as a function of the energy of the lowest π^* MO in the complex. A linear regression is obtained, with a correlation coefficient $\rho = 0.971$ for nine data points. If one attempts similar correlations between the same observable (H-3) chemical shift and the energy of other MOs in the complex, one meets with the expected success. But the correlations are somewhat less impressive. Another test is that of the correspondence between the results for crotonaldehyde—which, following Childs et al.⁹, was picked as the test molecule—and other α,β -unsaturated carbonyls. We plot in Figure 3 the correlation between the values for the lowest π^* MO in crotonaldehyde and in methyl acrylate. This correlation is excellent ($\rho = 0.999$ for eight data points).

Justification of the NMR Method. Let us start with carbon-13 chemical shifts. They are dominated by the paramagnetic term.¹⁴ This paramagnetic term originates in the mixing under imposition of the B_0 magnetic induction field of excited states with the electronic ground state.¹⁵ Accordingly, carbon-13 chemical shifts are predicted to be inversely proportional to an average excitation

**Figure 3.** Correlation between the two lowest π^* MOs (eV) of Lewis acid-methyl acrylate complexes (ordinate) and Lewis acid-crotonaldehyde complexes (abscissa).**Figure 4.** Chemical shift variations for the C-3 carbon in crotonaldehyde as a function of the electronic charge on the carbon.

energy (in the closure approximation).¹⁵ Indeed, there is experimental evidence correlating variations in the ¹³C chemical shifts and the electronic excitation energies.¹⁶ In the example of crotonaldehyde and of the chemical shift for the C-3 carbon, one thus expects a rough linear dependence of the chemical shift on the reciprocal of the energy gap between the HOMO and the LUMO.

Another description is the empirical dependence of ¹³C chemical shifts on the electronic charge at carbon. Since the classical paper by Spiess and Schneider,¹⁷ complemented by Grant and Michl by their determination of the individual components of the shielding tensor,¹⁸ numerous authors have reported or made use of chemical shift-charge correlations with slopes of ca. 180 ppm per electron.¹⁹ Accordingly, it is no surprise if the C-3 chemical shift⁹ correlates with the electronic charge at carbon that we calculate by MNDO (Figure 4; correlation coefficient 0.998 for five points).

Less expected was the quality of the correlations between, on one hand, the electronic charges at C-3 and at H-3 (correlation coefficient 0.979 for 12 points) and, on the other hand, the chemical shift of the H-3 proton and the electric charge on the H-3 proton (correlation coefficient 0.975 for 9 points).

These are the reasons for the success of the measurement of Lewis acidity by the NMR method of Childs et al.⁹ It is rather unexpected that proton chemical shifts, predominantly diamagnetic, with a limited sensitivity, should do such a fine job, especially

(16) Savitsky, G. B.; Nawikawa, K.; Zweifel, G. *J. Phys. Chem.* **1965**, *69*, 3105-3109.

(17) Spiess, H.; Schneider, W. G. *Tetrahedron Lett.* **1961**, 468-472.

(18) Strub, H.; Beeler, A. J.; Grant, D. M.; Michl, J.; Cutts, P. W.; Zilm, K. W. *J. Am. Chem. Soc.* **1983**, *105*, 3333-3334.

(19) Hallden-Abberton, M.; Fraenkel, G. K. *Tetrahedron* **1982**, *38*, 71-74.

(14) Ramsey, N. F. *Phys. Rev.* **1950**, *78*, 699-703.

(15) (a) Pople, J. A. *Mol. Phys.* **1964**, *7*, 301-306. (b) Karplus, M.; Pople, J. A. *J. Chem. Phys.* **1963**, *38*, 2803-2807.

when consideration is restricted to the trace of the tensor whose physical significance is not obvious.

Some Problems of the NMR Method. The method of Childs et al.⁹ has considerable merit: it is one of the very few available measurements of the strength of a Lewis acid interacting with an α,β -unsaturated carbonyl. Nevertheless, it suffers from some drawbacks. These are both experimental and theoretical. A big problem in implementing the Childs method⁹ is residual humidity because of the Lewis acid sensibility to water. The requirement for total dryness makes the Childs et al. method⁹ somewhat less practical. Because of the likely presence of some humidity, the chemical shift measurement can *underestimate* the strength of the Lewis acid. And the relative error will be biggest for the weakest Lewis acids.

Another cause for concern is the possibility of chemical reactions between the Lewis acid and the solvent. An example that has been considered recently in a study of catalysis of the Diels-Alder reaction by Lewis acids¹⁰ is α elimination from methylene chloride. If such a process is significant, it produces small quantities of the chloromethylene carbene:CHCl, of protonated crotonaldehyde, and of tetrachloroaluminate $AlCl_4^-$. The measurement of the H-3 chemical shifts thus is doubly in error: because some of the Lewis acid molecules have been inactivated, and because of protonation of the probe molecule. The latter factor cannot be underestimated; the proton decreases the π^* MO much more than Lewis acids (a factor 3-6). However, it is not possible to evaluate the error in the apparent strength of a Lewis acid from the chemical shift measurement in the presence of traces of protic acids; extrapolation of the $q(H-3)$ vs π^* regression (Figure 6) does not go through the point representative of H^+ .

Yet another possible artifact may arise with chlorinated solvents. Unless special care is taken (storage in dark bottles and treatment with bicarbonate prior to use), they may contain hydrochloric acid resulting from photochemical reactions between moisture and the solvent. The joint presence of protons and chloride ions would have a similar effect as that of protons and of aluminate ions.

A fourth factor that complicates practical use of the attractive method of Childs et al.⁹ is the need for sufficient solubility of the Lewis acid to be measured in methylene chloride, the solvent in which this experimental scale⁹ is defined. To pick out one very important example, zinc chloride²⁰ has very weak solubility at best in methylene chloride. Obviously, for a scale of Lewis acidities to hold, the concentration of the Lewis acids has to be uniform.

Likewise, use of gaseous Lewis acids (such as BF_3 or the alkylaluminums) runs against the problem of the accurate determination of their concentration in the methylene chloride solution.

Stoichiometry of the complexes is yet another question. Childs et al.⁹ used an excess of the Lewis acid to ensure that the crotonaldehyde probe is 100% in the complexed form. In addition, one should be wary of the possibility of a fallacious determination of a Lewis acidity if the chemical shift of a 1:1 complex (between crotonaldehyde and Lewis acid LA_1) is compared directly with that for a 2:1 complex (between crotonaldehyde and Lewis acid LA_2). There are such cases, and the NMR method,⁹ when combined with the titration over the appropriate range of the relative concentrations is very nicely suited to their detection. To take the example of tin tetrachloride, we find titration of crotonaldehyde by variable amounts of $SnCl_4$ to be consistent with 2:1 (rather than 1:1) complex formation (Figure 5). Two molecules of crotonaldehyde bind to the tin metal.

Another difficulty with the NMR method lies in its basis. The implicit postulates are, first, a proportionality between the Lewis acidity and the increment of positive charge generated at C-3 and, second, another proportionality between the positive charge at C-3 and the chemical shift of the H-3 proton. While the linear 1H - ^{13}C correlations reported by Childs et al.⁹ are consonant with the latter,

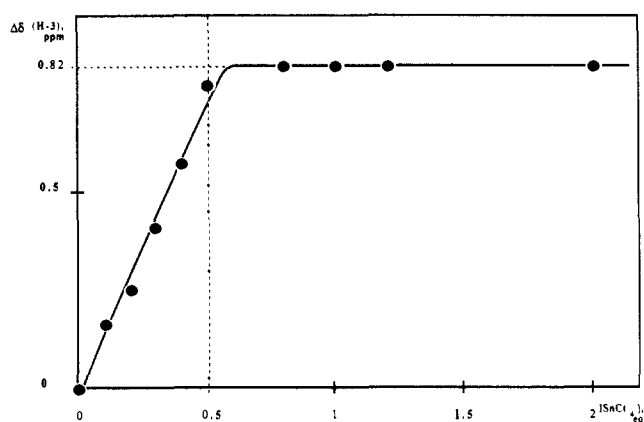


Figure 5. Titration of crotonaldehyde by tin tetrachloride in methylene chloride solution at 20 °C.

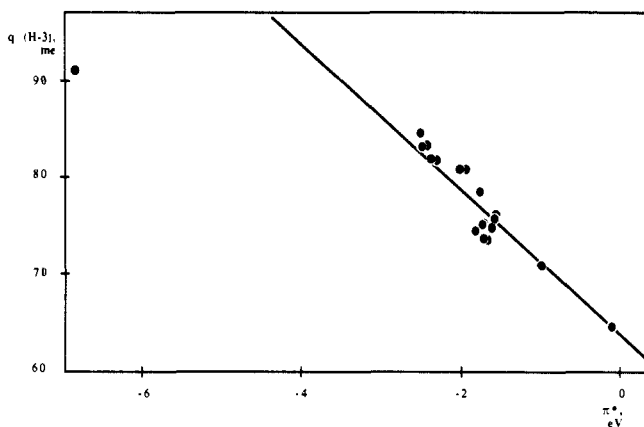


Figure 6. Plot of the calculated charge at H-3 (me) as a function of the energy (eV) of the lowest π^* -type MO in the complex.

the former is more in the nature of an act of faith. Other factors known to be important in determining chemical shifts, such as diamagnetic anisotropy, van der Waals interactions, and the reaction field,²² are neglected. The Childs group⁹ was well aware of this deficiency and commented indeed that "it is possible that local anisotropy effects are important in determining the chemical shift of H-1 in the Lewis acid complexes".⁹

Some Advantages of the Molecular Orbital Method. A first gain from the MNDO calculations is thus an improved justification for the experimental NMR method.⁹ We find that the postulate of a linear change in the charge development at H-3 and the attendant chemical shift is supported by a correlation of the MNDO calculated position for the π^* level with the calculated charge on the H-3 proton (Figure 6). Indeed, the finding of a correlation between the calculated values for the π^* level and the observed chemical shift for H-3 in the complex (Figure 3) follows logically from Figure 6.

Another plus is that of any calculation. It allows access to molecular systems that are impractical, for one reason or another. An example is that of aluminum hydride, AlH_3 , whose formation requires treatment of lithium aluminum hydride, $LiAlH_4$, with 100% sulfuric acid in THF,²³ another is that of mercury(II) derivatives, seldom used because of their toxicity.

Yet more complex cases are amenable to calculation. As an example, we determined the Lewis acidity of $AlMeOPh_2$. This compound can be considered a model for more complex organoaluminum species recently used by Yamamoto et al.^{7b} for catalysis

(20) Zinc chloride is a Lewis acid which, while of low intrinsic activity as a Friedel-Crafts catalyst,⁸ becomes an outstanding catalyst after impregnation on a clay support.²¹

(21) (a) Clark, J. H.; Kybett, A. P.; Macquarie, D. J.; Barlow, S. J.; Landon, P. *J. Chem. Soc., Chem. Commun.* **1989**, 1353-1354. (b) Cornélis, A.; Gerstmans, A.; Laszlo, P.; Mathy, A.; Zieba, I., submitted for publication.

(22) (a) Laszlo, P.; Stang, P. *Organic Spectroscopy*; Harper and Row: New York, 1971. (b) Laszlo, P.; Musher, J. I. *J. Chem. Phys.* **1964**, *41*, 3906-3911.

(23) Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry*, 5th ed., Wiley-Interscience: New York, 1988; p 221.

(24) Lappert, M. F. *J. Chem. Soc.* **1962**, 242-248.

(25) Satchell, D. P. N.; Satchell, R. S. *Chem. Rev.* **1969**, *69*, 251-278.

of the Claisen rearrangement. The Childs NMR method⁹ is not applicable to this particular Lewis acid, because of overlap of the resonances for the aromatic and for the H-3 proton.

We list in the table the sequence of Lewis acidities toward crotonaldehyde as obtained by the present MO method for ca 20 Lewis acids. A first check is its applicability to other α,β -unsaturated carbonyls as Lewis bases. The generality of the method appears to be borne out by the correlation shown in Figure 2, in which the lowering of the π^* level for methyl acrylate is seen to be linearly related to that for crotonaldehyde as the probe substance.

Conclusion

We have provided a method, simple to implement, giving direct access to a quantitative determination of the strength of a Lewis

acid. It may usefully complement the array of existing experimental methods for estimating these Lewis acidities, such as Gutmann acceptor numbers,²⁶ the IR determination of Lappert,²⁴ or the astute NMR method by Childs⁹ that was the springboard for our study.

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(26) Gutmann, V. *Coordination Chemistry in Non-Aqueous Solutions*; Springer-Verlag: New York, 1968.

The Application of Nuclear Quadrupole Resonance to the Study of Clathrates. ³⁵Cl NQR and Crystallography of Clathrated CCl₄

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Abstract: The ³⁵Cl nuclear quadrupole resonance (NQR) spectra of CCl₄ in more than 20 clathrates have been measured in the range 4–200 K. The crystal structures of CCl₄/Dianin's compound (1), CCl₄/Fe(AcAc)₃ (3), CCl₄/Ni(SCN)₂(3-MePy)₄ (4), and CCl₄/Ni(exan)₂(4,4'-dm-2,2'-bpy) (19) clathrates are also reported. Site symmetry and site multiplicity of the guest molecule in clathrates were determined by NQR spectroscopy and by X-ray crystallography. The degree of host-guest interaction was estimated from the NQR frequency shifts. The libration frequencies of the guest molecules in trigonal cavities were determined from NQR frequencies by Bayer-Kushida theory analysis.

Introduction

Clathrates, or more generally *inclusion compounds*, possess two essential components: the first, *the host molecule*, forms a solid lattice characterized by lacunae in which can be included the second component, *the guest molecule*. The intermolecular interactions between these two components are usually very weak compared to a normal chemical bond.

Various physical methods¹ have been used in the study of clathrates and inclusion compounds. Previously, we have briefly reported² the applications of the nuclear quadrupole resonance to the study of small guest molecules in different clathrate systems.

Since the electronic field gradient tensor at a nucleus in a molecule depends strongly upon the molecular structure, the nuclear quadrupole interaction offers a sensitive probe which may be used to study inclusion compounds and to obtain information on the following points: (1) site symmetry, (2) site multiplicity, (3) host-guest interaction, (4) guest molecule mobility, (5) molecular disorder, (6) the existence of different clathrate phases, and (7) phase transitions.

Some of the information given by NQR spectra can be confirmed by X-ray structure analysis. Thus, these two physical methods are complementary in studies of clathrates and inclusion compounds.

Although Dianin's compound, Ni(SCN)₂(3-MePy)₄, and Fe(AcAc)₃ complexes are well-known to form clathrates with a great

variety of substances and the structures of the chloroform clathrates were previously described,^{3–5} their CCl₄ clathrates have never been studied by physical methods, and the crystal structures were unknown. CCl₄ is, however, in our experience, a very appropriate probe molecule in this context since its high symmetry avoids disorder of the guest molecule in the cavities and its high chlorine content increases the inherent sensitivity of the ³⁵Cl NQR method. We have therefore used this guest molecule as a probe for studying different clathrate systems by NQR and X-ray structure analysis.

Experimental Section

Preparations. All host compounds, except ferric acetylacetonate which was a commercially available product, were prepared according to literature methods and characterized by their mass spectra (Finnigan 4023, energy of the ionizing beam, 70 eV) and their ¹H NMR spectra (Varian XL100) or by elemental analyses. The clathrates were prepared by recrystallization of the appropriate hosts from CCl₄ as solvent and characterized by using either elemental analyses, thermogravimetric analysis, or, for complexes with known crystal structure, density mea-

(1) *Inclusion Compounds*; Atwood, J. L., Davies, J. E. D., MacNicol, D. D., Eds.; Academic Press: London, 1984; Vol. 3, Physical Properties and Applications.

(2) Pang, L.; Lucken, E. A. C. *J. Incl. Phenom.* **1987**, *5*, 245.

(3) Flippen, J. L.; Karle, J.; Karle, I. L. *J. Am. Chem. Soc.* **1970**, *92*, 3749.

(4) Nassimbeni, L. R.; Papanicolaou, S.; Moore, M. H. *J. Incl. Phenom.* **1986**, *4*, 31.

(5) Steinbach, J. F.; Burns, J. H. *J. Am. Chem. Soc.* **1958**, *80*, 1839.

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