# Chemical and Spectroscopic Studies Related to the Lewis Acidity of Lithium Perchlorate in Diethyl Ether

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Polarimetric studies on camphor (**2**) as well as IR studies on crotonaldehyde (CA; **1**) and benzonitrile (BN; **3**) confirm the conclusion of a previously published NMR study on crotonaldehyde that lithium perchlorate (LP) weakly binds to probe bases in diethyl ether (DE). The weak binding is a consequence of the fact that the lithium ion (actually the LP ion pair and higher aggregates), a powerful Lewis acid in the gas phase, competitively binds to ether and the added base. Methylene camphor (**5**), (*E*)-1,3-pentadiene (**4**), camphene, and phenylacetylene (**6**) do not bind to LP in DE. Shifts to lower energy of the C═O modes of CA in ether solutions containing increasing amounts of LP are consistent with moderate increases in solvent polarity. Only small or no shifts are seen in the C≡N modes of BN and its 1:1 complex with added LP. Because the C≡N and especially C═O modes are blue shifted under external applied pressure, the large internal pressures of LP/DE do not mimic external applied pressure. Likewise, the small or no changes observed in $\lambda_{max}$ for the absorption and emission spectra of anthracene (**9**) and azulene (**8**) in ether as a function of LP concentration do not conform to what is observed under external applied pressure. Studies of the Diels−Alder reaction of (*E*)-1,3-pentadiene with methyl acrylate show that the reaction is entirely catalyzed in LP/DE; polarity and internal pressure do not influence product selectivity in this reaction.

## Introduction

Lithium perchlorate in diethyl ether (LP/DE) has become a widely used medium in organic synthesis, particularly for what are formally pericyclic reactions.[1] The mode by which this solvent does its work, however, has become a source of controversy and uncertainty. Consider the following points. (1) Pocker has shown that LP in DE has a very large accelerating effect on reactions that yield ions, e.g., $S_N1$ reactions.[2−8] He attributed these rate enhancements to electrostatic catalysis in which the large Coulomb fields of the ions stabilize polar transition states. Much of these data can also be rationalized by mechanisms in which the lithium ion functions as a Lewis acid catalyst. (2) On the basis of how LP/DE and hydrostatic (applied) pressure ($P_a$) influence Diels−Alder (DA) reactions in general and the DA reaction of furan with 2,5-dihydrothiophene-3,4-dicarboxylic anhydride in particular, which is used in the total synthesis of cantharidin,[9] Grieco made the novel suggestion[10] that adding LP to DE increases the internal pressure ($P_i$) of the solvent,[11] which then mimics the effect that $P_a$ has on reactions. Kumar determined $P_i$ for LP/DE from thermodynamic and other data and showed that $P_i$ indeed goes up significantly as the concentration of LP in DE goes up.[12] Kumar also suggested on theoretical grounds that $P_i$ does mimic the effect that $P_a$ has on the rates of DA reactions. In fact the rates of the Diels−Alder reaction of *N*-methylmaleimide with anthracene-9-carbinol in aqueous salt solutions correlate nicely with internal pressure, but the internal pressure has only a minimal effect on rates.[13] Likewise, the dimerization of cyclopentadiene correlates with internal pressure, but the correlation is not very good.[14] Others have also shown experimentally that $P_i$ does not have the same effect on cycloaddition reactions as $P_a$ has;[15−17] its effect is at best quite small. (3) Braun and Sauer, on the other hand, have proposed that changes in product selectivity for the reactions of cyclopentadiene (CP) with methyl acrylate (MA) in LP/DE are due to changes in solvent polarity,[18] as one might expect when salts are dissolved in liquids.[11,19] Braun and Sauer in fact calculated Ω, a solvent polarity index devised by Berson[20] which is based on the CP/MA reaction, for the LP/DE salt solutions. Kiselev and

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[1] (a) Grieco, P. A. *Aldrichim. Acta* **1991**, *24*, 59. (b) Waldmann, H. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 1306. (c) Grieco, P. A. In *Organic Chemistry: Its Language and Its State of the Art*; Kisakürek, M. V., Ed.; VCH: Weinheim, 1993; p 133. (d) Flohr, A.; Waldmann, H. *J. Prakt. Chem.* **1995**, *37*, 609.

[2] Pocker, Y.; Buchholz, R. F. *J. Am. Chem. Soc.* **1970**, *92*, 2075.

[3] Pocker, Y.; Buchholz, R. F. *J. Am. Chem. Soc.* **1970**, *92*, 4033.

[4] Pocker, Y.; Buchholz, R. F. *J. Am. Chem. Soc.* **1971**, *93*, 2905.

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[6] Pocker, Y.; Ellsworth, D. L. *J. Am. Chem. Soc.* **1977**, *99*, 2284.

[7] Pocker, Y.; Ciula, J. C. *J. Am. Chem. Soc.* **1988**, *110*, 2904.

[8] Pocker, Y.; Ciula, J. C. *J. Am. Chem. Soc.* **1989**, *111*, 4728.

[9] Dauben, W. G.; Kessel, C. R.; Takemura, K. H. *J. Am. Chem. Soc.* **1980**, *102*, 6894.

[10] Grieco, P. A.; Nunes, J. J.; Gaul, M. D. *J. Am. Chem. Soc.* **1990**, *112*, 4595.

[11] Reichardt, C. *Solvents and Solvent Effects in Organic Chemistry*, 2nd ed.; VCH: Weinheim, 1988.

[12] Kumar, A. *J. Org. Chem.* **1994**, *59*, 4612.

[13] Kumar, A. *Pure Appl. Chem.* **1998**, *70*, 615.

[14] Reference 11, p 193.

[15] Dauben, W. G.; Lam, J. Y. L.; Guo, Z. R. *J. Org. Chem.* **1996**, *61*, 4816.

[16] Faita, G.; Righetti, P. P. *Tetrahedron* **1995**, *51*, 9091.

[17] Jenner, G.; Salem, R. B. *Tetrahedron* **1997**, *53*, 4637.

[18] Braun, R.; Sauer, J. *Chem. Ber.* **1986**, *119*, 1269.

[19] Loupy, A.; Tchoubar, B. *Salt Effects in Organic and Organometallic Chemistry*; VCH: Weinheim, 1992.

[20] Berson, J. A.; Hamlet, Z.; Mueller, W. A. *J. Am. Chem. Soc.* **1962**, *84*, 297.

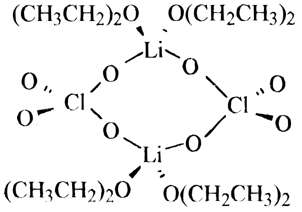
10.1021/jo981042x CCC: $18.00

co-workers arrived at a conclusion similar to that of Braun and Sauer based on the kinetics of several (4+2)-, (3+2)-, and (2+2)-cycloaddition reactions.[21] In one (3+2)-cycloaddition the rate was actually *slower* in LP/DE than in DE because one of the polar reactants was stabilized by the polar LP/DE more than the transition state was.[21] (4) A still different perspective was given by Pagni, Kabalka, et al., who showed using chemical, spectroscopic, and theoretical data that LP in DE functions as a mild Lewis acid, i.e., catalyst, with the strong Lewis acidity of $Li^+$ being abated in part by competitive complexation to DE.[22] Kinetic studies are also consistent with LP functioning as a catalyst.[16,23]

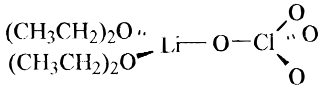
Several other properties of LP in DE should be mentioned, as they may also have a bearing on the various mechanisms of “catalysis” described above. On the basis of the measurements of conductivity and viscosity of LP/DE, Ekelin and Sillén in the 1950s proposed that LP in ether is aggregated (ion pairs and higher aggregates) and the lithium ions are, in addition, complexed to an unknown number of ether molecules.[24] In the early 1970s Pocker demonstrated by $^1$H NMR spectroscopy[2] that each lithium ion is in fact bound to two ether molecules in solutions up to 4.25 M in LP, the concentration at which all the ether is complexed and the solution becomes a molten salt;[25] between 4.25 and 6.00 M, where saturation is reached, the molten salt becomes progressively richer in lithium ions bound to one ether.[2] Somewhat later Ménard and Chabanel proved using dielectric measurements that LP ion pairs exist primarily in dimers (eq 1) at low concentrations of LP in

$$2\mathrm{LiClO_4} \rightleftharpoons (\mathrm{LiClO_4})_2 \qquad K = 650\ \mathrm{M}^{-1} \qquad (1)$$

DE (<0.1 M) at 20 °C.[26] Presumably at higher LP concentrations, higher aggregates of LP exist. Thus, if each lithium ion is complexed to two ether molecules and also exists in an LP dimer at low LP concentration, a picture emerges in which each lithium ion in the dimer exists in a tetrahedral environment, as shown below.



The monomeric LP ion pair can be detected as well by IR and Raman spectroscopy. On the basis of how the complexing lithium ion perturbs the tetrahedral perchlorate anion away from ideal symmetry, Chabanel and co-workers showed in 1996 that the anion functions as a monodentate ligand.[27] Thus, the structure of the ion pair, at least at low LP concentration, is



Neither of these structures—and others for the larger aggregates—should be envisioned as static, however. There is clearly a rapid interchange of the ions in the various structures as well as the complexed ethers with those in the solvent. LP in ether must contain therefore an admixture of ion pairs and higher aggregates, all in rapid equilibrium and whose composition depends on the initial concentration of LP.

We have now carried out a new set of experiments, largely different in character from those reported in our earlier work,[22] to assess the catalytic power of LP in DE. We wish to report the results of these experiments at this time. We hope these new results, and those published earlier, will give a new perspective on the competing roles of catalysis, polarity, and internal pressure of LP/DE in organic reactions.

## Results and Discussion

One way to assess the importance of catalysis to reactions occurring in LP/DE is to see if LP binds to species with lone pairs of electrons, and how strongly. To see why this is important consider the LP-catalyzed DA reaction of MA with CP to form product (P) (actually endo and exo adducts) which requires three steps: (1) the reversible binding of LP to MA; (2) the DA reaction of the complex with CP; and (3) the reversible binding of the product to LP.

$$\mathrm{MA} + \mathrm{LP} \overset{K_e}{\rightleftharpoons} \mathrm{MA{\cdot}LP}$$

$$\mathrm{MA{\cdot}LP} + \mathrm{CP} \xrightarrow{k_2} \mathrm{P{\cdot}LP}$$

$$\mathrm{P{\cdot}LP} \underset{K_e'}{\rightleftharpoons} \mathrm{P} + \mathrm{LP}$$

The rate of formation of the product and its complex is given by[28]

$$\frac{\mathrm{d}[\mathrm{P}]}{\mathrm{d}t} + \frac{\mathrm{d}[\mathrm{P{\cdot}LP}]}{\mathrm{d}t} = k_{\mathrm{obs}}[\mathrm{CP}][\mathrm{MA}][\mathrm{LP}]$$

where $k_{\mathrm{obs}} = k_2K_e$.[29,30] Thus the magnitude of the binding of the Lewis acid to the dienophile directly influences any rate acceleration for the DA reaction. The rate acceleration is also influenced by the magnitude of $k_2$, whose value depends on how effectively the Lewis acid lowers the LUMO of the dienophile,[31] and also the intrinsic reactivity of the diene.

The molecules initially chosen for spectroscopic study were (*E*)-2-butenal (**1**; CA = crotonaldehyde), a model

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[21] Shtyrlin, Y. G.; Murzin, D. G.; Luzanova, N. A.; Ishkakova, G. G.; Kiselev, V. D.; Konovalov, A. I. *Tetrahedron* **1998**, *54*, 2631.

[22] (a) Pagni, R. M.; Kabalka, G. W.; Bains, S.; Plesco, M.; Wilson, J.; Bartmess, J. *J. Org. Chem.* **1993**, *58*, 3130. (b) Bains, S.; Pagni, R. M.; Kabalka, G. W.; Pagni, R. M. *Tetrahedron Asymmetry* **1994**, *5*, 821.

[23] Forman, M. A.; Dailey, W. P. *J. Am. Chem. Soc.* **1991**, *113*, 2762.

[24] Ekelin, K.; Sillén, L. G. *Acta Chem. Scand.* **1953**, *7*, 987.

[25] Solutions below 4.25 M may also be considered a molten salt if one considers $\mathrm{Li(Et_2O)_2}^+$ $\mathrm{ClO_4}^-$ to be the solvent and ether the solute.

[26] Ménard, D.; Chabanel, M. *J. Phys. Chem.* **1975**, *79*, 1081.

[27] Chabanel, M.; Legoff, D.; Touaj, K. *J. Chem. Soc., Faraday Trans.* **1996**, *92*, 4199.

[28] This expression is preferred to that for d[P]/d*t* because the latter one will contain terms in $K_e'$ which are not relevant to the present discussion.

[29] If the uncatalyzed Diels–Alder reaction competes with the catalyzed reaction, an unusual situation but one that occurs here when CP is the diene (this is addressed later in the paper), the rate expression will contain an additional term. This does not occur, even in LP/DE, when less reactive dienes are used.

[30] There are, of course, other limiting cases. For instance, if the binding of Lewis acid and dienophile is fast and essentially irreversible, a common situation, $k_{\mathrm{obs}} = k_2$ because one is measuring the rate for the reaction of the complex with the diene.

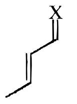
[31] Isaacs, N. S. *Physical Organic Chemistry*; Longman: Essex, 1987; p 704.

**Table 1. Equilibrium Constants for the Reaction of Bases with LP in DE**[a]

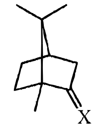
| base (B) | nature of complex: B·LP[b] | nature of complex: $B_2$·LP[c] | method | ref |
|---|---|---|---|---|
| Reichardt's dye | $5.0 \times 10^6$ | | UV/vis | 8 |
| 8,9-diacetylsesquifulvene | 18.2[d] | 7.10[e] | UV/vis | 8 |
| 8,9-dibenzoylsesquifulvene | 15.8[d] | 7.77[e] | UV/vis | 8 |
| 8,9-diformylsesquifulvene | 16.8 | | UV/vis | 8 |
| 8,9-dicarbomethoxysesquifulvene | | 7.39 | UV/vis | 8 |
| *N,N*-diethylindoaniline | *f* | | UV/vis | 8 |
| crotonaldehyde | 3.20[g] | | $^1$H NMR | 22a |
| menthone | 7.3 | | polarimetry | 4 |
| camphor | 4.95 | | polarimetry | this work |
| methylene camphor | 0 | | polarimetry | this work |
| crotonaldehyde | 8.7 | | IR | this work |
| (*E*)-1,3-pentadiene | 0 | | IR | this work |
| benzonitrile | 0.71 | | IR | this work |
| phenylacetylene | 0 | | IR | this work |

[a] Determined at room temperature. [b] $K_{eq}$/M$^{-1}$. [c] $K_{eq}$/M$^{-2}$. [d] Seen at high [LP]. [e] Seen at low [LP]. [f] $K_{eq}$ could not be determined. [g] Determined at −20 °C.

base used in the study of Lewis acidity,[32] optically active camphor (**2**), and benzonitrile (**3**; BN), all of which are weakly basic. Similar studies were also carried out on the all-carbon analogues of these bases: (*E*)-1,3-pentadiene (**4**; *trans*-piperylene), methylene camphor (**5**),[33] and phenylacetylene (**6**). Additional experiments were also carried out on acetone (**7**), azulene **(8)**, and anthracene **(9)**.



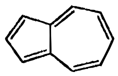
**1** X = O
**4** X = $CH_2$



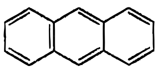
**2** X = O
**5** X = $CH_2$

PhC≡X

**3** X = N
**6** X = CH



**8**



**9**

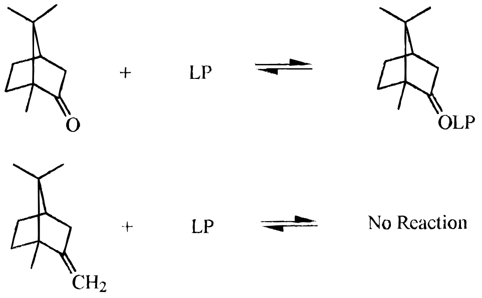
Several prior attempts have been made to study (quantitatively) the binding of probe bases (Bs) to LP in DE by various spectroscopies (Table 1).[4,8,22a] In none of the reported cases was the complex seen directly; it was only "detected" by inference based on assumptions used to fit the spectral data to a model. Considering the complexity of LP in DE, as described earlier, the majority of cases, remarkably, fit the simplest model: $B + LP \rightleftharpoons B{\cdot}LP$.

Similar to that reported previous for optically active menthone,[4] the binding of camphor to LP in DE was studied polarimetrically (Table 2), fitting the changes in optical rotation to a mathematical model reported in a previous publication in which the binding of crotonaldehyde to LP was studied by $^1$H NMR.[22a] The fit was surprisingly good considering that optical rotations are solvent dependent, and there is a large difference in solvent properties on going from pure ether to 1.90 M LP in ether. The fit yielded $K_{eq}$(camphor) = 4.95, a value similar to that for menthone (Table 1). By contrast, the rotation of methylene camphor, the all-carbon analogue of camphor, remained constant at −48.4 ± 0.3° in solutions from 0.125 to 1.50 M in LP. Clearly LP does not bind to the alkene. Surprisingly, there is also no measurable solvent effect on the optical rotation of this compound.[34]

**Table 2. Optical Rotations of Camphor in LP/DE**

| initial concn: $[camphor]_0$ | initial concn: $[LP]_0$ | rotations: observed[a] | rotations: theory[b] |
|---|---|---|---|
| 0.534 | | +4.24 | +4.24 |
| 0.535 | 0.0981 | +4.05 | +4.06 |
| 0.535 | 0.250 | +3.56 | +3.56 |
| 0.534 | 0.503 | +3.08 | +3.07 |
| 0.529 | 1.001 | +2.43 | +2.57 |
| 0.539 | 1.904 | +2.25 | +2.29 |

[a] Taken in a 1 dm cell at +21 °C at the sodium D line. [b] Assumes $K_{eq}$ = 4.95 and the rotation of camphor minus the rotation of complex = −2.22°.



Direct detection of the contributing components would verify the UV/vis, NMR, and chirooptical results and give, in addition, information on how the species respond to changes in solvent properties. IR spectroscopy is well suited for these purposes. One, of course, can detect chromophores such as nitrile and carbonyl groups by their distinctive stretching frequencies. Complexation of these groups often leads to new stretching frequencies, and species in dynamic equilibrium are often seen by IR when they are not by other spectroscopies.

CA (0.100 M) in DE has a carbonyl stretching vibration at 1699 cm$^{-1}$. When LP at low concentration (0.0400–0.100 M) is incorporated into this solution, a new band at 1687 cm$^{-1}$ grows in at the expense of the CA band

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

(33) Clase, J. A.; Li, D. L. F.; Lo, L.; Money, T. *Can. J. Chem.* **1990**, *68*, 1829.

(34) The optical rotations of camphene also remained constant in DE containing 0–2M LP.

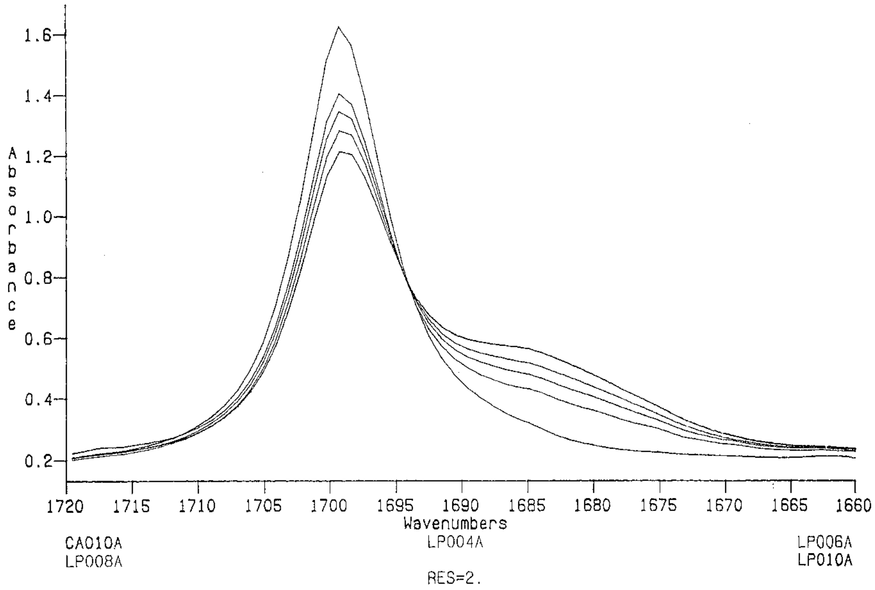

**Figure 1.** IR spectra of crotonaldehyde in LP/DE, carbonyl region at low LP concentration.

**Table 3. Curve-Fitting Results (Lorentzian Line Shape) for CA in LP/DE,[a] Low-Concentration Regime**

| | CA band | | | CA·LP band | | |
|---|---|---|---|---|---|---|
| $[LP]_0$ | $\lambda_{max}{}^{b}$ | WHH$^{b,c}$ | area | $\lambda_{max}{}^{b}$ | WHH$^{b,c}$ | area |
| 0 | 1699 | 8.38 | 18.53 | | | |
| 0.0400 | 1699 | 7.57 | 13.41 | 1687 | 28.87 | 7.27 |
| 0.0600 | 1699 | 7.56 | 12.72 | 1686 | 24.33 | 8.19 |
| 0.0800 | 1699 | 7.59 | 11.98 | 1686 | 23.15 | 9.44 |
| 0.100 | 1699 | 7.79 | 11.39 | 1685 | 20.70 | 9.86 |

[a] $[CA]_0 = 0.100$ M. [b] In cm$^{-1}$. [c] Width at half-height.

**Table 4. Calculation of $K_{eq}$ for CA + LP Reaction[a]**

| | at equilibrium | | | |
|---|---|---|---|---|
| $[LP]_0$ | [CA][b] | [CA·LP][c] | [LP][d] | $K_{eq}$ |
| 0.0400 | 0.0723 | 0.0279 | 0.0121 | 31.9 |
| 0.0600 | 0.0686 | 0.0314 | 0.0286 | 16.0 |
| 0.0800 | 0.0646 | 0.0362 | 0.0438 | 12.8 |
| 0.100 | 0.0614 | 0.0378 | 0.0622 | 9.9 |

[a] $[CP]_0 = 0.100$ M; $\epsilon_{CA} = 23780$ and $\epsilon_{CA\cdot LP} = 33445$; $d = 0.00780$ cm. [b] $[CA] = A_{CA}/\epsilon_{CA}d$. [c] $[CA\cdot LP] = A_{CA\cdot LP}/\epsilon_{CA\cdot LP}d$. [d] $[LP] = [LP]_0 - [CA\cdot LP]$.

(Figure 1). The new band at lower energy is due to the carbonyl stretch of the CP·LP complex. It is well-known that complexation of a Lewis acid to an aldehyde or ketone results in a carbonyl vibration at lower energy.[35] MNDO calculations on CA and CA·LP yield the expected shift, although the calculated magnitude is much larger than what is observed (90 cm$^{-1}$ vs 12 cm$^{-1}$).[36]

$$CA + LP \xrightleftharpoons{K_{eq}} CA\cdot LP$$

Because the system is well behaved at low [LP], i.e., yielding an isosbestic point between the two bands, it is possible to calculate $K_{eq}$ for the reaction. One way to do this requires knowledge of the areas under the two bands. This was accomplished by a curve-fitting routine assuming the bands had Gaussian, Lorentzian, or Pearson line shapes. Only two bands were required to give very good fits ($r \approx 0.99$) for all three line shapes. The results, which are shown in Table 3 for the Lorentzian line shape, reveal that $\lambda_{max}$(CA) remains constant while $\lambda_{max}$(CA·LP) changes very slightly, with the difference in peak positions being 12−14 cm$^{-1}$.[37] As expected for a well-behaved two-component system, eq 2, where $A_{CA}$ and $A_{CA\cdot LP}$ are the areas under the bands, $d$ is the cell length (determined by the interference fringe method [38]), $[CA]_0$ is the initial concentration of CA, and $\epsilon_{CA}$ and $\epsilon_{CA\cdot LP}$ are the respective integrated extinction coefficients, is obeyed ($r = 0.993$).[39]

$$\frac{A_{CA\cdot LP}}{[CA]_0} = \epsilon_{CA\cdot LP}d - \left(\frac{\epsilon_{CA\cdot LP}}{\epsilon_{CA}}\right)\left(\frac{A_{CA}}{[CA]_0}\right) \qquad (2)$$

The slope and intercept of eq 2 yield the two extinction coefficients ($\epsilon_{CA\cdot LP} > \epsilon_{CA}$) and thus $K_{eq}$ (Table 4). Surprisingly, $K_{eq}$ goes down as $[LP]_0$ goes up ($\log K_{eq} = 1.19 \pm 0.12$). This behavior often arises when a third (or more) component is present in the system.[39] This is not the case here, however, because factor analysis,[40] which is a mathematical procedure designed specifically to identify the number of components in a system, shows that only two components, CA and CA·LP, are required to fit the data for the titration of CA by LP in DE, with $\log K_{eq} = 0.94 \pm 0.11$.[41−43] This value is subject to some uncertainty because the titration is only 30% complete. One cannot

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(35) Cassimatis, D.; Susz, B. P. *Helv. Chim. Acta* **1960**, *43*, 852.

(36) A better model for a complex might have been an adduct of the LP ion pair with CA. One would also expect to see a shift in the carbonyl stretching frequency to lower energy, but not as much as for the CA·Li$^{+}$ complex.

(37) The results were essentially the same for all three line shapes.

(38) Nakanishi, K. *Infrared Absorption Spectroscopy*; Holden-Day: San Francisco, 1964.

(39) (a) Bulmer, J. T.; Shurvell, H. F. In *Vibrational Spectra and Structure*; Durig, J. R., Ed.; Elsevier: Amsterdam, 1977; Vol. 6; p 91. (b) McBryde, W. A. E. *Talanta Rev.* **1974**, *21*, 979.

(40) Harman, H. H. *Modern Factor Analysis*, 3rd ed.; University of Chicago: Chicago, 1976.

(41) It is not clear why the more direct method gives a seemingly less precise estimate of $K_{eq}$ than factor analysis even though the data fit eq 1 nicely. In fact the $K_{eq}$ values and the error limits are not appreciably different.

(42) These $K_{eq}$ values, and many in Table 1, assume that all the LP is in the form of the LP ion pair, which is not the case. If one takes into account the fact that $2LP \rightleftharpoons (LP)_2$, with $K_{eq} = 650$ M$^{-1}$ at the $LP_0$ concentrations used here, the calculated equilibrium constant comes out about an order of magnitude larger.

**Table 5. IR Data for CA[a] in LP/DE, Higher Concentrations Regime**

| | CA | | CA·LP | |
|---|---|---|---|---|
| $[LP]_0$ | $\lambda_{max}$[b] | WHH[b] | $\lambda_{max}$[b] | WHH[b] |
| 0.100 | 1699 | 7.79 | 1686 | 20.70 |
| 0.300 | 1696 | 10.06 | 1682 | 16.37 |
| 0.600 | 1694 | 11.06 | 1680 | 15.08 |
| 1.00 | 1692 | 11.96 | 1680 | 14.70 |
| 2.00 | 1688 | 12.27 | 1679 | 13.90 |
| 3.00 | 1687 | 11.65 | 1680 | 11.75 |

[a] $[CA]_0 = 0.100$ M. [b] In $cm^{-1}$.

use data beyond this point in the calculation for reasons that will be come apparent shortly. Interestingly $K_{eq}$(CA) is not appreciably different in value from those obtained for other bases in LP/DE using other spectroscopic techniques.

As the solutions become still richer in LP, $A_{CA}$ continues to decrease and $A_{CA\cdot LP}$ increases, as expected for the reversible reaction of CA with LP. However, one is no longer justified in using the areas to calculate $K_{eq}$. First of all, the Beer–Lambert law breaks down because band areas now also correlate with increasing solvent polarity, which we believe is occurring as LP is added to DE (vide infra). Published data show that the integrated absorption intensity (area) for the C═O mode of CA (at constant concentration) increases significantly as solvent polarity goes up.[44] Second, although no new C═O modes are observed at higher LP concentrations, the isosbestic point disappears between the CA and CA·LP bands because $\lambda_{max}$(CA) and $\lambda_{max}$(CA·LP) shift to lower energy and the line widths change as well (Table 5).

The causes for the changes in line widths are unknown but may be due to environmental influences on lifetime and dephasing of the vibrational excited states.[45] Line width may also change when new LP–CA complexes are formed at higher LP concentrations and old complexes disappear.

The $\lambda_{max}$'s of both CO stretching modes shift to lower energy as the LP concentration in DE increases The shift in CA's mode is a consequence of an increase in the polarity of LP/DE, as reflected, for example, in the increase in the dielectric constant of the medium. Similar behavior has been observed for $Ba(ClO_4)_2$ in *N*,*N*-dimethylacetamide.[46] As further proof that this is so, the CO stretching mode of acetone (A) in 18 solvents correlates nicely with the solvents' $E_T(30)$ values; that is, the mode goes down in energy as the polarity of the solvent goes up.[47] $E_T(30)$ is an empirically derived measure of solvent polarity.[11] On the basis of this correlation and the behavior of CA's CO mode in LP/DE, 1.00 M LP/DE has a polarity similar to that for $CH_3CN$ and DMF, while 3.00 M LP/DE has a polarity similar to that of ethanol and formamide.

**Table 6. IR Data for Acetone[a] in LP/DE**

| $[LP]_0$ | $\lambda_{max}$ $(cm)^{-1}$ | amplitude |
|---|---|---|
| 0 | 1719.5 | 0.394 |
| 0.0992 | 1718.0 | 0.421 |
| 0.151 | 1717.1 | 0.436 |
| 0.207 | 1716.4 | 0.465 |
| 0.247 | 1716.0 | 0.481 |
| 0.297 | 1715.7 | 0.518 |
| 0.401 | 1715.2 | 0.572 |
| 0.750 | 1714.3 | 0.637 |
| 1.001 | 1713.9 | 0.743 |

[a] $[acetone]_0 = 0.100$ M.

The change in $\lambda_{max}$ for the CO mode of the complex is more difficult to interpret. The shifts here may also be a reflection of the change in the polarity of the medium. They may also be due to the build up of new complexes with CO stretching vibrations at lower energy and the synchronous decay of the CO mode for LP·CA at higher energy. Although there is no evidence for this from the shapes of the peaks, this would be consistent with changes in the widths of the peaks. In an attempt to resolve this issue, acetone's CO stretching vibration was also studied by IR in LP/DE (Table 6; Figure 2). Surprisingly, acetone yielded only a single peak in LP/DE whose $\lambda_{max}$ went to lower energy as the LP concentration increased. Peak amplitudes and widths simultaneously increased. One may surmise that acetone is not binding to LP, but this is unlikely. A more reasonable interpretation, one that is generally believed by researchers in this area,[8,46] is that there are undetected, but overlapping bands for acetone and its LP complex. With this premise in mind it was possible to fit acetone's spectral data to the model used by Pocker[8] to analyze the visible spectra of dyes in LP/DE. The analysis yielded $K_{eq} = 1.9 \pm 0.3$ for $A + LP \rightleftharpoons A\cdot LP$.[48] Thus, because the A and A·LP bands are not resolved, the spectral data are not helpful in resolving the origin of the $\lambda_{max}$ shifts of the CO stretching mode of LP·CA.

Unlike the C═O mode of CA, the C═C mode at 1640 $cm^{-1}$ does not change position or line width in DE as the concentration of LP is increased.[49] Likewise, the two C═C stretching modes of (*E*)-1,3-pentadiene (**4**) at 1611 and 1647 $cm^{-1}$ do not undergo changes in line position and minimal changes in line width and amplitude in LP/DE. There are thus no bonding or through-space interactions between the diene and LP in DE.

Benzonitrile (BN) also binds to LP in DE. The C≡N stretching mode for BN at 2228 $cm^{-1}$ is systematically replaced by a new C≡N mode at higher energy[50] (~2255 $cm^{-1}$) as the concentration of LP in DE is increased. This new mode arises from the BN·LP adduct.[50] Unlike the C═O mode for CA in LP/DE, the C≡N mode for BN does not change position and minimally changes line width in LP/DE (Table 7).[51] The C≡N mode for BN·LP, on the other hand, changes position (to lower energy) and line

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[43] It is not clear if $Et_2O$ is displaced by CA. If it is, one should take this fact into account in calculating the equilibrium constant. However, because the concentration of $Et_2O$ in LP/DE is so much higher than the concentration of $Et_2O$ displaced in the reaction, one can assume that $[Et_2O]$ is constant and, thus, can be ignored in the equilibrium expression.

[44] Brunn, J.; Beck, C. *Z. Chem.* **1984**, *24*, 222.

[45] Bradley, M. S.; Bratu, C. *J. Chem. Educ.* **1997**, *74*, 553.

[46] Baron, M. H.; Jaeschke, J.; Moravie, R. M.; De Lozé, C.; Corset, J. In *Metal–Ligand Interactions in Organic Chemistry and Biochemistry*; Pullman, B., Goldblum, N., Eds.; Reidel: Dortrecht, 1977; Part 1; p 171.

[47] (a) Pagni, R. M. Unpublished results based on data taken from ref 11. (b) The correlation is $E_T = -1.593\lambda_{max} + 2771$ ($r = 0.943$). (c) If one includes $PhNH_2$ and $D_2O$, both of which can donate two H bonds, in the analysis, the correlation is not quite as good ($r = 0.907$).

[48] Our model assumes (1) that the A and A·LP carbonyl bands do not change wavelengths and (2) that the spectrum in 1 M LP/DE largely is due to the complex.

[49] MNDO calculations predict a shift of 48 $cm^{-1}$ for the C═C mode when CA is complexed to $Li^+$ .

[50] Complexation of Lewis acids to nitriles in solution, solid state, and crystal results in an adduct having a C≡N mode at higher energy due to shortening of the C–N bond length: Beattie, I. R.; Jones, P. *J. Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 1527. Jiao, H. Schleyer, P. v. R. *J. Am. Chem. Soc.* **1994**, *116*, 7429.

[51] Phenylacetylene, the all-carbon analogue of benzonitrile, has a C≡C stretching mode at 2110 $cm^{-1}$, whose position changes by no more than 1 $cm^{-1}$ on going from DE to 1.50 M LP in DE.

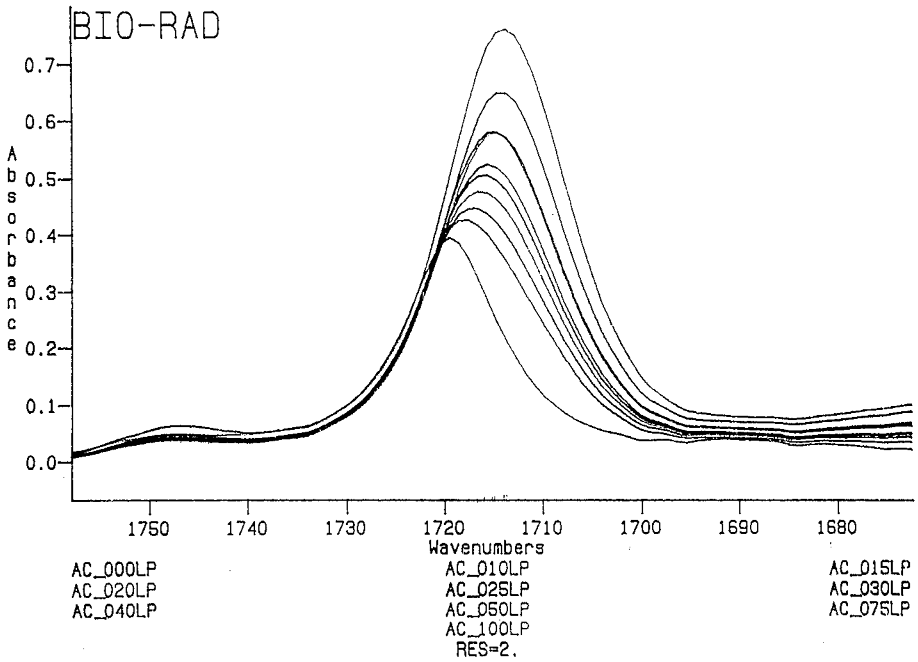

**Figure 2.** IR spectra of acetone in LP/DE, carbonyl Region.

**Table 7. Curve-Fitting Results (Lorentzian Line Shape) for BN[a] in LP/DE**

| | BN band | | | BN·LP band | | |
|---|---|---|---|---|---|---|
| $[LP]_0$ | $\lambda_{max}$[b] | WHH[b,c] | area | $\lambda_{max}$[b] | WHH[b,c] | area |
| 0 | 2228 | 11.63 | 4.67[d] | | | |
| 0.200 | 2228 | 12.26 | 3.07 | 2264 | 29.40 | 4.13 |
| 0.300 | 2228 | 12.01 | 4.32 | 2257 | 22.21 | 3.63 |
| 0.450 | 2228 | 12.33 | 3.46 | 2256 | 22.19 | 4.12 |
| 0.600 | 2228 | 11.79 | 3.91 | 2256 | 20.40 | 5.71 |
| 1.00 | 2228 | 11.46 | 3.37 | 2254 | 19.24 | 8.42 |
| 2.00 | 2228 | 11.52 | 2.18 | 2253 | 18.40 | 11.79 |

[a] $[BN]_0 = 0.285$ M. [b] In cm$^{-1}$. [c] WHH = width at half-height. [d] $\epsilon_{BN} = A_{BN}/[BN]_0 d = 2100$.

width. It is because of these changes that a genuine isosbestic point is not observed between the two C≡N bands (Figure 3). Nonetheless, it was still possible to obtain $K_{eq}$ from the peak areas.

$$BN + LP \rightleftharpoons BN{\cdot}LP$$

To adequately curve-fit the two C≡N bands, it was necessary to include in the procedure two ether peaks that flanked the two C≡N bands (Figure 4). The data obtained at $[LP]_0 = 0.100$ M were excluded from the calculations because the BN·LP and ether modes are weak and broad and, as a result, difficult to deconvolute, and they give anomalous results.[52] From the resultant areas (Table 8), the integrated extinction coefficients for BN and BN·LP were derived, and thus $K_{eq}$ (Table 8). One thus gets a consistent set of $K_{eq}$ values all the way up to 2.00 M LP in DE, an extraordinary result ($K_{eq} = 0.71$; $\log K_{eq} = -0.147 \pm 0.014$).

The previously reported NMR studies on CA[22a] and the current polarimetry studies on camphor and IR studies on CA and BN (and acetone) confirm that LP in ether binds to aldehydes, ketones, and nitriles. Alkenes, on the other hand, show no evidence of complexation. The extent of binding, as measured by equilibrium constants, is relatively small even though $Li^+$ is a superior Lewis acid. This is a consequence of the facts that $Li^+$ is ion paired to $ClO_4^-$ in ether and the probe bases compete for LP. Changes in $\lambda_{max}$ as a function of LP concentration are consistent with modest increases in solvent polarity as the medium becomes richer in LP. The IR studies provide no evidence that the well-established internal pressures of LP/DE solutions[12] mimic applied external pressure. Carbonyl and nitrile stretching modes are blue shifted under applied pressure,[53] which is not seen in LP/DE. Shifts of up to 15 cm$^{-1}$ are seen for ketones under 10 kbar of external pressure, a value numerically similar to the internal pressure of 3 M LP in DE.

There are even more dramatic data that show that internal pressure does not mimic applied or external pressure. It is well-known that the positions of absorption and emission bands for benzenoid and nonbenzenoid hydrocarbons are often very sensitive to external pressure. Thus, if the internal pressure of LP/DE mimics applied pressure, as suggested by Grieco[10] and Kumar,[12,13] one will be able to predict where the absorption and fluorescence spectra will occur for the hydrocarbons in LP/DE if the behavior of the hydrocarbons in solution under external pressure has been established.

To test this idea the first absorption band of anthracene and its fluorescence band and the second absorption band of azulene and its fluorescence band were examined in DE as a function of LP concentration. These data, as well as the predicted band positions, are recorded in Table 8. Although the emission behavior of azulene is nicely predicted by the internal pressure argument, its absorption behavior is not. Furthermore, the experimental and predicted absorption bands of anthracene are dramatically different. Experimentally the 0−0 band shifts 2 nm to the red on going from DE to 5.0 M LP in DE; the predicted shift is 52 nm. Even though the predicted shifts may be lower than listed in

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[52] Note, for example, the anomalous $\lambda_{max}(BN{\cdot}LP)$ value at $[LP]_0 = 1.00$ M. Calculation of $K_{eq}$ from the $[LP]_0 = 0.100$ M numbers also afforded a value of $K_{eq}$ out of line with the other $K_{eq}$ values.

[53] Wiederkehr, R. R.; Drickamer, H. G. *J. Chem. Phys.* **1958**, *28*, 311.

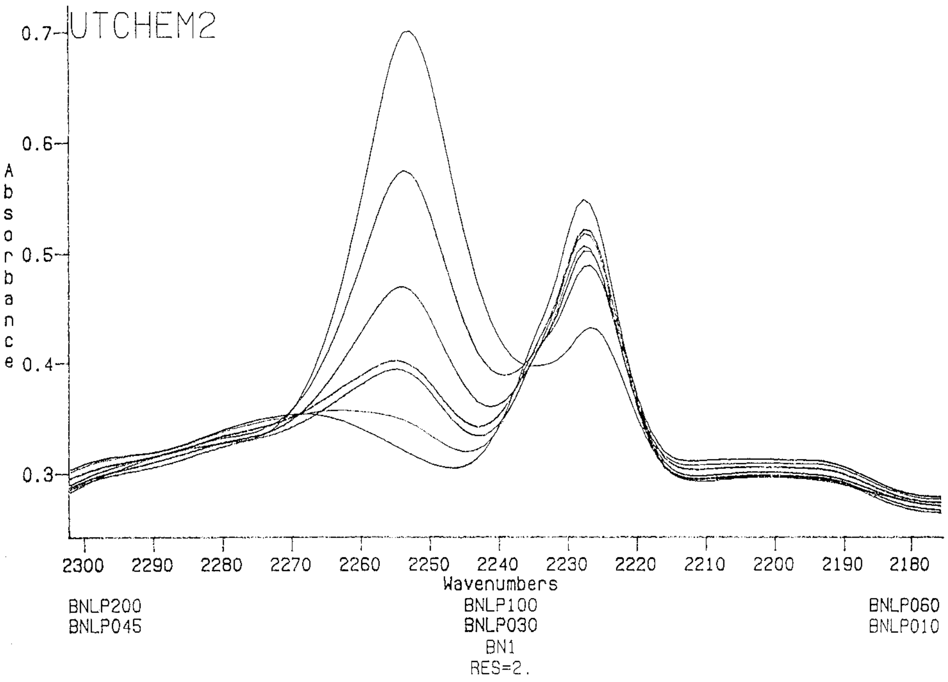

**Figure 3.** IR spectra of benzonitrile in LP/DE, nitrile stretching region.

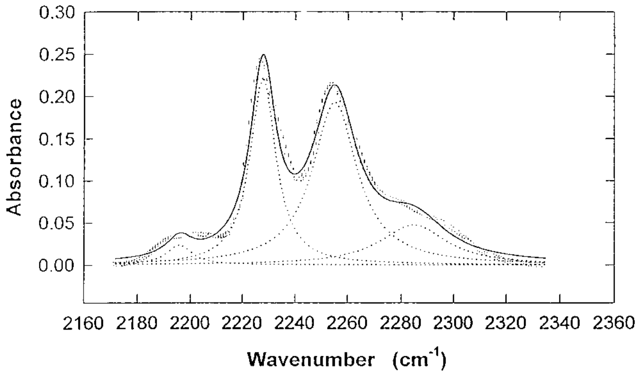

**Figure 4.** Curve fitting of two C≡N and two ether bands: (solid line) experimental; (■) computer fit; (dashed line) computer-generated spectra of individual bands.

**Table 8. Calculation of $K_{eq}$ for BN + LP Reaction**[a,b]

| | at equilibrium | | | |
|---|---|---|---|---|
| $[LP]_0$ | [BN][c] | [BN·LP][d] | [LP][a,c] | $K_{eq}$ |
| 0.100 | 0.239 | 0.0425 | 0.0575 | (3.1) |
| 0.300 | 0.251 | 0.0502 | 0.250 | 0.80 |
| 0.450 | 0.201 | 0.0570 | 0.393 | 0.72 |
| 0.600 | 0.227 | 0.0790 | 0.521 | 0.69 |
| 1.00 | 0.195 | 0.117 | 0.883 | 0.68 |
| 2.00 | 0.126 | 0.163 | 1.84 | 0.70 |

[a] $[BN]_0 = 0.285$ M. [b] $\epsilon_{BN} = 2210$ and $\epsilon_{BN \cdot LP} = 9260$. These were determined by the method described in the text using all data except that at $[LP]_o = 0.100$ M. [c] $[BN] = A_{BN}/\epsilon_{BN}d$. [d] $[BN \cdot LP] = A_{BN \cdot LP}/\epsilon_{BN \cdot LP}d$. [e] $[LP] = [LP_0] - [BN \cdot LP]$.

**Table 9. Absorption and Emission Data for Anthracene and Azulene in LP/DE**

| | anthracene (0−0 band in nm) | | | | azulene (0−0 band in nm) | | | |
|---|---|---|---|---|---|---|---|---|
| | absorption | | emission | | absorption | | emission | |
| [LP] | expt | theory[a] | expt | theory[b] | expt | theory[c] | expt | theory[d] |
| 0.0 | 376 | 376 | 381 | | 352 | 352 | 354 | 354 |
| 0.5 | 376 | 378 | 383 | | 352 | 353 | 355 | 354 |
| 1.0 | 376 | 381 | 380 | | 352 | 354 | 355 | 354 |
| 2.0 | 376 | 388 | 382 | | 352 | 356 | 356 | 355 |
| 4.0 | 378 | 410 | 382 | | 352 | 358 | 357 | 356 |
| 5.0 | 378 | 428 | 382 | | 352 | 360 | 357 | 357 |

[a] Based on $-203$ cm$^{-1}$ kbar shift in pentane (refs 54 and 55). [b] No suitable data available. [c] Based on a $-40$ cm$^{-1}$ kbar shift in pentane (refs 54 and 55). [d] Based on a $-15$ cm$^{-1}$ kbar shift in methyl methacrylate polymer (refs 54 and 56).

Table 9 because the shifts under applied pressed are solvent dependent[54] and some shifts level off at higher applied pressure,[55a] there can be no doubt that the calculated shifts would still be much larger than those observed in fact. This demonstrates again that internal pressure does not mimic applied pressure.

Finally, let us return to Braun's and Sauer's contention, mentioned earlier in the paper, that changes in the polarity of LP/DE are responsible for changes in the diastereoselectivity of Diels−Alder reaction of cyclopentadiene with methyl acrylate.[18] These results tacitly assume that this reaction is uncatalyzed, which seems unlikely on the basis of the results presented in this paper. Had internal pressure mimicked applied pressure, the changes in diastereoselectivity could have been explained as well because the two product-forming reactions have different activation volumes, but this idea has now been discredited. In an earlier publication, Pagni, Kabalka, and co-workers provided a more credible and unique explanation.[22b] In their model the catalyzed and uncatalyzed reactions, each giving a different ratio of products, compete in LP/DE, with the catalyzed reaction becoming more dominant as the LP concentration goes up. The competition is a consequence of having a reactive diene (CP)[57] and a small catalytic acceleration, i.e.,

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(54) Isaacs, N. S. *Liquid-Phase High-Pressure Chemistry*; Wiley: Chichester, 1981; Chapter 6.

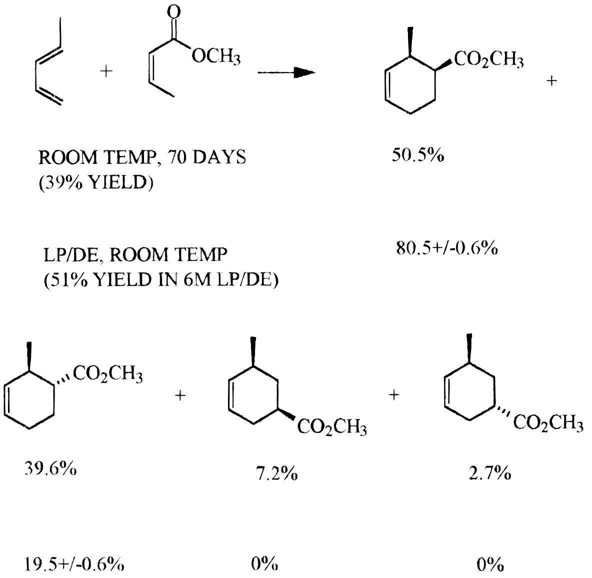
(55) (a) Robertson, W. W.; Weiging, O. E.; Matsen, F. A. *J. Mol. Spectros.* **1957**, *1*, 1. (b) Robertson, W. W.; King, A. D. *J. Chem. Phys.* **1961**, *34*, 1511.

(56) Mitchell, D. J.; Drickamer, H. G.; Schuster, G. B. *J. Am. Chem. Soc.* **1977**, *99*, 7489.

(57) Kiselev, V. D.; Konovalov, A. I. *Russ. Chem. Rev.* **1989**, *58*, 230.

$k_{cat}/k_{uncat}$. For the reaction of CP with dimenthyl fumarate, for example, which fits the model nicely, $k_{obs}(cat)/k_{obs}(uncat) = 2.58$.[58] Braun's and Sauer's data for the MA + CP reaction, which also fit the Pagni−Kabalka model well, yield $k_{obs}(cat)k_{obs}(uncat) = 14$.[59]

If one had a Diels−Alder reaction in which the catalytic accelerating effect is large, product selectivity would be invariant, provided that polarity and internal pressure were not important. This may occur by "slowing down" the uncatalyzed reaction by using unreactive dienes such as furan and (*E*)-1,3-pentadiene.[57] The published reaction of (aromatic) furan with 2,5-dihydrothiophene-3,4-dicarboxylic anhydride[10] does not occur thermally but does in LP/DE, yielding a constant ratio of adducts from 1 to 5 M LP in DE. Likewise, the reaction of (*E*)-1,3-pentadiene with MA is exceptionally slow at room temperature[60] but in LP/DE is greatly accelerated,[61] yielding essentially the same product distribution from 1 to 6 M LP in DE.



## Conclusions

These studies confirm our earlier published hypothesis that LP functions as a weak Lewis acid in DE. There is no evidence that the large internal pressures of LP/DE mimic applied external pressure.

## Experimental Section

**Instruments.** Gas chromatography (GC) was performed using a Hewlett-Packard 5890 GC instrument equipped with a 30 m × 1/8 in. column packed with 30% SE-30 by weight on a Chromosorb W support. Gas chromatography with mass spectrometry was performed using a Hewlett-Packard 5890 GC with a 5970 mass spectrometer.

Nuclear magnetic resonance (NMR) spectra were obtained on Bruker AC 250 and 400 MHz spectrometers. Samples were dissolved in $CDCl_3$ with 1% tetramethylsilane (TMS) as the internal standard ($\delta = 0.0$ ppm).

The polarimetric data were collected using a Perkin-Elmer M421 polarimeter. This is an automatic polarimeter with optical null balance and automatic gain control. Readings were taken at 21 °C. A continuous sodium discharge lamp was used as a light source. The instrument was set at an integration time of 5 s for all readings. A standard glass cell with a path length of 1 dm and a capacity of 6.2 mL was used for all work.

**Chemicals.** The chemicals were of the highest quality and used as received. Methylene camphor was prepared by a literature procedure.[33] Lithium perchlorate obtained from Aldrich Chemical Co. was dried under a high-vacuum over $P_2O_5$ for 24 h in a drying piston. Ethylene glycol (bp 196−198 °C) was the refluxing solvent in the pot. The $LiClO_4$ was kept in a desiccator over calcium chloride until it was ready for use. All manipulations involving the use of $LiClO_4$ were done rapidly under open air conditions.

Crotonaldehyde solutions were prepared by first preparing a 2.85 M stock solution of crotonaldehyde in diethyl ether. This solution was prepared by adding 2.36 mL of crotonaldehyde (density = 0.856 g/cm$^3$) by syringe to a 10 mL volumetric flask and then diluting to the mark with diethyl ether. From this stock solution 1 mL aliquots were taken via a 1 mL pipet and then transferred to a 10 mL volumetric flask to which was subsequently added the appropriate molar amount of $LiClO_4$. Diethyl ether was then added to the mark with periodic shaking. After all the $LiClO_4$ dissolved, the solutions were then transferred to 10 mL Wheaton vials, which were then septum sealed and crimped. The solutions were kept in these vials until they were ready for FTIR analysis. Other solutions were prepared in a like manner.

**Acquisition and Spectral Manipulation of IR Data.** Before filling, the sealed NaCl cells were first cleaned once with spectroscopic grade acetone and then with anhydrous diethyl ether. The cell was then dried using a clean inert air duster (Enviro. Ro. Tech, Duster 1671) from Tech Spray Inc.

The solution to be analyzed was removed by syringe through the Wheaton vial's septum seal. After allowing a copious amount of the solution to flow through the cell, it was capped and the outside thoroughly cleaned with acetone. This was necessary in order to remove traces of $LiClO_4$ which became deposited on the cell and its windows.

All data were acquired on either a Bio-Rad FTS-60 A or a FTS-7 Fourier transform infrared spectrometer. Each spectrometer is controlled by a computer with an Idris operating system, which is a UNIX-like operating system, and the FTS 3200 data station, which is the software installed on the Winchester hard drive. The software acquires and stores all the data into files. Data were acquired at a resolution of 2 cm$^{-1}$ for 64 scans. The IR cell used to measure the absorbancies of the other solutions was a precision-amalgamated flow through cell which consisted of a lead spacer between sodium chloride plates. Luer-Lock fittings with Teflon seals permitted filing and draining the cell via Luer-Lock syringes. The cell path length, *b*, was computed by the interference fringe method for the empty cell using the following equation:

$$b = \frac{1}{2D}\left(\frac{n}{\nu_1 - \nu_2}\right)$$

where $n$ is the number of fringes (successive maxima or minima) between two wavenumbers $\nu_1$ and $\nu_2$ and $D$ is the refractive index of the sample material (1.5443 for NaCl).

The addition of lithium perchlorate to ether solutions of crotonaldehyde resulted in the appearance of a new band in the carbonyl stretching region which overlapped with the uncomplexed band. Similarly, a new band overlapping the nitrile stretching band appeared when lithium perchlorate was added to ether solutions of benzonitrile. To curve-fit the bands, portions of the original files were transferred to MS-DOS format and imported into DOS software packages on an IBM 386 computer. Additional Bio-Rad software was acquired for this purpose. First, a 240 cm$^{-1}$ interval centered about the band of interest was extracted from the original data file using the "zap" programm which creates a temporary truncated

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[58] The reaction of the very reactive 9,10-dimethylanthracene with acrylonitrile in LP/DE shows a small catalytic acceleration of 2.2: Forman, M. A.; Dailey, W. *J. Am. Chem. Soc.* **1991**, *113*, 2761. This is based on the linear plot of $k_{obs}$ versus [LP], where $k_{obs} = k_{uncat} + k_{cat}$[LP].

[59] Pagni, R. M. Unpublished results.

[60] (a) Inukai, T.; Kojima, T. *J. Org. Chem.* **1967**, *32*, 869. (b) Inukai, T.; Kojima, T. *J. Org. Chem.* **1966**, *31*, 1121.

[61] The catalytic rate acceleration is ∼140.

spectrum. To create the temporary file, the following command was typed at the % command prompt: % Zap-trunc-startHINO-stopLONO DATAFILE.DT temp, where HINO refers to the higher wavenumber of the interval, LONO refers to the lower wavenumber of the interval, DATAFILE.DT is the data file being truncated, and temp is the name of the temporary truncated file. A second Bio-Rad program, "dtdumb2", converts the temps file into an ASCII text file. A third Bio-Rad program, "cp2pc", converts the Bio-Rad text file into a MS-DOS text file on floppy disk. Once stored on the floppy disk, the file was imported into a Jandel Scientific Software package called "Peakfit". In Peakfit, the absorbance bands were first baseline corrected and then curve fitted. Several fit options were available for the data required here; both the Lorentzian and Pearson routines appeared to give the best correlation coefficients and the lowest standard deviations.

**Diels−Alder Reaction of (*E*)-1,3-Pentadiene and Methyl Acrylate in the Presence of 6 M $LiClO_4$.** To a 10 mL flame-dried volumetric flask containing 6.40 g of lithium perchlorate (60.0 mmol) was added 3 mL of anhydrous diethyl ether. Methyl acrylate (0.33 mL, 3.7 mmol) was added by syringe. The volumetric flask was filled with ether to its mark. The solution was shaken to dissolve the lithium perchlorate, then transferred via a double-ended needle to a septum-sealed, flame-dried test tube equipped with a magnetic stirrer. The mixture was left to stir for 12 h at room temperature. The solution was then first washed with water (2 × 10 mL), then neutralized with 5% sodium bicarbonate solution (2 × 10 mL), and finally concentrated in vacuo. Products were compared to independently made compounds. Analysis was accomplished via $^1$H and $^{13}$C NMR spectroscopy and GC. GC yield: 40% yield of ortho-endo; 11% yield of ortho-exo. No meta-endo and meta-exo adducts were formed.

Reactions with different concentrations of LP in DE were run similarly.

**MO Calculations.** The molecular orbital (MO) calculations were carried out on a SPARC server 1000 workstation using MOPAC 6 (QCPE 581). The input geometries were obtained from molecular mechanics calculations using PCMODEL (Serena Software), 4th edition.

**Absorption and Fluorescence Measurements and Calculations.** Absorption spectra were recorded on a Hewlett-Packard 8452A diode array spectrophotometer, and fluorescence spectra were recorded on an Aminco-Bowman Series 2 luminescence spectrometer. Internal pressures of LP/DE were calculated by the method of Kumar.[12] To predict how a band should shift if internal pressure mimics external pressure, the following equation was used: Shift in $cm^{-1}$ = (known shift under external pressure in $cm^{-1}$ $kbar^{-1}$) (internal pressure of LP/DE in kbar − internal pressure of pure ether in kbar). The reported shifts for the absorption spectra of azulene in pentane under applied pressure were reported against density of the solvent.[55b] To correct these data into spectral shifts versus kbars of applied pressure, the published data on the density of pentane versus applied pressure were used.[62]

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(62) Danforth, W. E., Jr. *Phys. Rev.* **1931**, *38*, 1224.