

Fourier Transform Ion Cyclotron Resonance Determination of Lithium Cation Basicities by the Kinetic Method: Upward Extension of the Scale to Phosphoryl Compounds

Erwin Buncel,¹ Austin Chen,¹ Michèle Decouzon,² Sally Ann Fancy,² Jean-François Gal,^{2*} Marta Herreros² and Pierre-Charles Maria²

¹ Department of Chemistry, Queen's University, Kingston, Ontario, K7L 3N6, Canada

² Groupe FT-ICR, GRECFO-Chimie Physique Organique, Université de Nice–Sophia Antipolis, 06108 NICE Cedex 2, France

Lithium cation basicities (*LCBs*) are reported for a series of 16 phosphoryl compounds, including phosphine oxides, phosphinates, phosphonates and phosphates. The experiments were carried out using the kinetic method applied to Fourier transform ion cyclotron resonance mass spectrometry. Two different data treatments of the Napierian logarithm of ion peak intensity ratios were compared: extrapolation to zero kinetic energy and weighted averaging of data over the range of energies studied. The effect of pressure on the *LCB* determinations was also studied. An increase in the pressure of the collision gas allows one to decrease the collision energy necessary for efficient dissociation of the lithium-bonded dimer, thus favoring the fragmentation pathway of lowest energy. Among the monofunctional ligands, the phosphoryl derivatives studied have the largest *LCBs* yet known. The previously published self-consistent *LCB* scale of Taft and co-workers was extended upward by 14 kJ mol⁻¹. © 1998 John Wiley & Sons, Ltd.

KEYWORDS: Fourier transform ion cyclotron resonance; lithium cation basicity; kinetic method; pressure effect; phosphoryl compounds

INTRODUCTION

Metal cation chemistry has been the subject of a number of recent reviews.¹ This interest originates from the important role that metal ions, in particular alkali metal ions, play in many reactions,² including those of biochemical interest, and in mass spectrometry, in the detection and determination of structures of organic compounds.³

One of the first steps in the understanding of the behavior of these ions in condensed media is to investigate the elementary processes in the gas phase, at the molecular level. Although experimental⁴ and theoretical⁵ information is available concerning the interaction of isolated molecules with Li⁺, there is a paucity of experimental data relative to the lithium cation basicity (*LCB*) of organophosphorus derivatives,

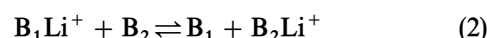
in particular of phosphoryl (P=O containing) compounds.

The aim of the present work was to determine, by using Fourier transform ion cyclotron resonance (FT-ICR) mass spectrometry, the *LCBs* of a series of compounds of general formula R₁R₂R₃PO, i.e. phosphine oxides, phosphinates, phosphonates and phosphates. This study was initiated by the observation that Li⁺ catalyzes the nucleophilic attack of ethoxide ion at the phosphoryl center.^{1f,2c} The effect was analyzed in terms of Li⁺–ethoxide interaction in the reactant and Li⁺–phosphoryl interaction in the transition state. As a preliminary step for this study, semi-empirical calculations of the Li⁺ affinities for phosphoryl and sulfonyl compounds have been performed in our group.^{5j}

LCB and lithium cation affinity (*LCA*), correspond respectively to the Gibbs energy and enthalpy changes of the reaction



Most *LCB* values currently available^{4f} were obtained by measuring the equilibrium constant of lithium cation transfer reactions between two neutral bases B₁ and B₂:



* Correspondence to: J.-F. Gal, Groupe FT-ICR, GRECFO-Chimie Physique Organique, Université de Nice–Sophia Antipolis, 06108 Nice Cedex 2, France.

E-mail: gal@unice.fr

Contract/grant sponsor: NATO; Contract/grant number: CRG 931176.

Contract/grant sponsor: Spanish Ministry of Education (Dirección General de Enseñanza).

Equilibrium constants have been derived by monitoring ion abundances and partial pressures of neutral compounds. The application of this method is restricted to sufficiently pure, stable and volatile compounds. Furthermore, the equilibrium must not be disturbed by secondary reactions, such as the formation of ion-bonded clusters. This problem is particularly severe in the case of P=O containing compounds, which have a very low volatility and form the homo- and heterodimers $(B_1LiB_1)^+$, $(B_2LiB_2)^+$ and $(B_1LiB_2)^+$ very quickly. During the measurements of proton basicity of phosphoryl compounds, the rapid formation of proton-bonded dimers was also observed.⁶

Taking advantage of the formation of such ion-bonded clusters, Cooks *et al.*⁷ developed a method based on the dimer unimolecular dissociation, referred to as the 'kinetic method.' This dissociation can be spontaneous or induced by collision (CID). In the latter case, it is recommended to carry out CID at low energy. However, it is common perception that, as ions become larger, they are more difficult to activate and to dissociate, especially under low-energy conditions. This difficulty has been attributed to the distribution of internal excitation over a large number of vibrational states and to the inefficiency of the collisional activation process. This problem could be solved by the use of a higher excitation energy or a higher pressure of the target gas. The effect of the first factor was considered in our previous investigations,⁸ but we did not investigate the effect of varying the pressure. In the present work, we investigated the effect of the collision gas pressure on measurements by the kinetic method, and we present and discuss here the *LCB* values obtained for a series of phosphoryl compounds.

EXPERIMENTAL

Most of the chemicals were obtained commercially (Aldrich Chemical, Fluka Chemical) and were used without further purification other than degassing reactants by freeze-pump-thaw cycles in the spectrometer inlet system. $(PhO)(Ph)_2PO$, $(p-CF_3PhO)(Ph)_2PO$ and $(p-FPhO)(Ph)_2PO$ were synthesized at Queen's University (Kingston, Ontario, Canada).⁹ The FT-ICR spectrometer, based on an electromagnet (1.6 T) and a Bruker (Fällanden, Switzerland) CMS 47 console,¹⁰ has been described previously. Its use for *LCB* determinations has also been described in earlier publications.⁸ Briefly, mixtures of neutral bases (B_1 and B_2) were introduced in the spectrometer at nominal pressure of $(3-5) \times 10^{-5}$ Pa. The lithium cation, generated by laser ablation from a lithium-aluminum alloy,⁸ was allowed to react with the neutral gases for about 1.5 s. The principal reactions observed, at the mean temperature of the cell (338 K), only heated by the filament used for standard electron ionization, were the formation of the simple adducts B_1Li^+ and B_2Li^+ and the formation of the dimers $[B_1LiB_1]^+$, $[B_2LiB_2]^+$ and $[B_1LiB_2]^+$. The species of interest, $[B_1LiB_2]^+$, was carefully isolated using a series of ejection pulses, then accelerated by resonant excitation. As described previously,^{8a} we checked that after selection there was no fragmentation

in the absence of excitation. In the absence of collision during the excitation time the kinetic energy, $E_{k,lab}$, can be calculated according to

$$E_{k,lab} = q^2 E_0^2 t^2 / 8m \quad (3)$$

where q is the charge, t is the RF resonant excitation duration for collisional activation and m is the ion mass.

The radiofrequency electric field magnitude, E_0 , is calculated according to

$$E_0 = V_{0(p-p)} S_{E1}^1 / d \quad (4)$$

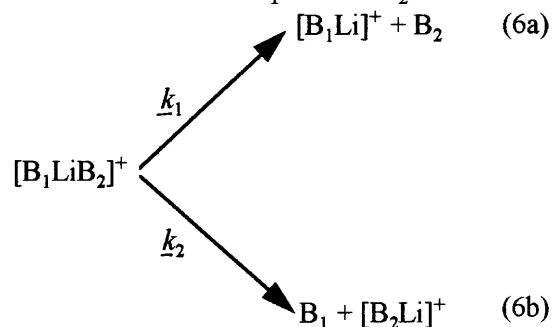
where $V_{0(p-p)}$ is the peak-to-peak voltage amplitude applied between the two excitation plates, d is the diameter of the cylindrical cell and S_{E1}^1 a first-order correction factor for the effective electric field taking into account the specific geometry of the system. The value $S_{E1}^1 = 0.808593$ is applicable in our case.⁸

The center-of-mass collision energy, $E_{k,cm}$, is calculated according to

$$E_{k,cm} = E_{k,lab} (M_{cg} / M_{cg} + M_{ion}) \quad (5)$$

where M_{cg} is the mass of the collision gas (argon in our case) and M_{ion} is the mass of the Li^+ -bonded dimer.

The calculated initial kinetic energy, in the center-of-mass frame, $E_{k,cm}$, was in the range 11–75 eV at low collision gas pressure (1×10^{-4} Pa) and 6–40 eV at high collision gas pressure (5×10^{-4} Pa). Within this range of kinetic energy and gas pressure, the probability of collision during the acceleration period is small (see below). After acceleration, the ion was allowed to collide with the neutral gases introduced in the cell (B_1 , B_2 and Ar as the collision gas) at static pressure (1×10^{-4} and 5×10^{-4} Pa) during a delay of 0.01–0.1 s. In most cases the only ions observed after fragmentation were the lithium-cationized monomers B_1Li^+ and B_2Li^+ :



Under certain conditions, during CID experiments on heterodimers containing $(ClCH_2)(EtO)_2PO$, $(EtO)_2MePO$, $(EtO)_3PO$ and $(i-PrO)_2HPO$, we observed the loss of ethylene and propene. Such a loss of neutral molecules has been observed previously in CID studies of organophosphorus compounds.¹¹ For $(i-PrO)_2HPO$, the loss of two propene molecules was also noticed. We did not utilize data pertaining to systems where these side fragmentations were significant, i.e. when the sum of the peak intensities of secondary fragments was larger than 15% of the precursor ion. For example, the dissociation of the Li^+ -bonded dimer of $(ClCH_2)(EtO)_2PO$ and $(i-PrO)_2HPO$ at low pressure and at $E_{k,cm} = 45$ eV gave the following spectrum: m/z 360 $[(i-PrO)_2HPOLiOP(EtO)_2(ClCH_2)]^+$, 100%; m/z 193 $[(ClCH_2)(EtO)_2POLi]^+$, 25.6%; m/z 173 $[(i-PrO)_2HPOLi]^+$, 34.0%, m/z 131 ($173 - C_3H_6$),

6.0%; m/z 89 ($173 - 2 \times C_3H_6$), 4.8% (31.8% fragmentation of the $[(i\text{-PrO})_2\text{HPOLi}]^+$ adduct).

The kinetic method makes use of the rates of unimolecular dissociation for estimating the relative bond dissociation energies.⁷ In the systems under scrutiny, this will translate into

$$\ln(k_1/k_2) = \ln[I(B_1\text{Li}^+)/I(B_2\text{Li}^+)] = \Delta E/RT \quad (7a)$$

Recent RRKM calculations by Brauman and co-workers¹² have shown the limits of application of the kinetic method. Not only the relative activation energies (supposed to represent relative dissociation energies), but also the relative entropies of activation, the size of the system and the degree of activation may influence the branching ratio. When all these effects are relatively constant or neglected, we arrive at

$$\ln(k_1/k_2) = \ln[I(B_1\text{Li}^+)/I(B_2\text{Li}^+)] \approx \Delta LCB/RT \quad (7b)$$

The various hypotheses underlying the derivation of Eqn (7b) may be a severe limitation to the application of the kinetic method. Nevertheless, the empirical validity of Eqn (7b) has been verified in our previous paper.^{8a}

The dissociation of the Li⁺-bonded dimers, according to Reaction (6), was monitored as a function of $E_{k,cm}$. Obviously, the best choice would be the study of all dissociations at the same energy. Unfortunately, this was not possible, owing to the widely different $E_{k,cm}$ necessary for dissociating significantly the different systems studied in the present work. In previous studies,⁸ we extrapolated $\ln[I(B_1\text{Li}^+)/I(B_2\text{Li}^+)]$ to zero $E_{k,cm}$ with the aim of standardizing all the measurements at the same energy. Nevertheless, we observed that the dependence of $\ln[I(B_1\text{Li}^+)/I(B_2\text{Li}^+)]$ on $E_{k,cm}$ was slight (within the collision energy range) and that the slopes of the regression lines were, in general, not significantly different from zero. Moreover, it appeared that the $[B_1\text{Li}B_2]^+$ ions formed from the organophosphorus compounds studied necessitate high energies for efficient dissociation, rendering extrapolations less reliable. Therefore, we decided to treat the data using the weighted (standard deviation) mean of $\ln[I(B_1\text{Li}^+)/I(B_2\text{Li}^+)]$ obtained at different $E_{k,cm}$. The lower limits of $E_{k,cm}$ (11 and 6 eV, at low and at high collision gas pressure, respectively) correspond to the smallest significant signals of the fragments. The upper limits (75 and 40 eV, respectively) are imposed by the observation of secondary fragmentations in some cases indicated above. $\ln[I(B_1\text{Li}^+)/I(B_2\text{Li}^+)]$ values were also extrapolated to zero $E_{k,cm}$ for comparison purposes.

Previous experiments⁸ were carried out at pressures of about of 1×10^{-4} Pa. Owing to the difficulty of dissociating the dimers of phosphoryl compounds at this pressure, we performed a systematic study using a higher pressure of the target gas. This study included compounds already reported in the previously published LCB scale.⁸

RESULTS AND DISCUSSION

Pressure effects and data treatment

The Napierian logarithms of the ion peak intensity

ratios, $\ln[I(B_1\text{Li}^+)/I(B_2\text{Li}^+)]$, were determined for a series of 33 compounds studied at two different collision gas pressures (1×10^{-4} and 5×10^{-4} Pa) referred to as 'low pressure' and 'high pressure' (see Table 1). The ICR cell temperature was 338 K. Two different data treatments, extrapolation to zero $E_{k,cm}$ and weighted averaging, were applied to the two sets of experiments. The corresponding data sets were referred to as 'intercept' and 'weighted mean', respectively. Then, the Napierian logarithms of the intensity ratios were combined to construct four comparative Li⁺ basicity ladders (relative to $i\text{-PrCN}$) with the aim of selecting the most reliable. For this purpose we correlated the 'intercept' vs. the 'weighted mean' data at 'low pressure,' Eqn (8), and at 'high pressure,' Eqn (9).

$$\begin{aligned} \ln \left[\frac{I(B_1\text{Li}^+)}{I(i\text{-PrCNLi}^+)} \right]_{\text{intercept}} &= (0.334 \pm 0.352) \\ &+ (0.975 \pm 0.043) \ln \left[\frac{I(B_1\text{Li}^+)}{I(i\text{-PrCNLi}^+)} \right]_{\text{weighted mean}} \quad (8) \\ r &= 0.9930, s = 0.44, n = 33 \end{aligned}$$

$$\begin{aligned} \ln \left[\frac{I(B_1\text{Li}^+)}{I(i\text{-PrCNLi}^+)} \right]_{\text{intercept}} &= (-0.105 \pm 0.327) \\ &+ (1.154 \pm 0.026) \ln \left[\frac{I(B_1\text{Li}^+)}{I(i\text{-PrCNLi}^+)} \right]_{\text{weighted mean}} \quad (9) \\ r &= 0.9983, s = 0.35, n = 28 \end{aligned}$$

where r is the correlation coefficient, s is the standard deviation of the residuals and n is the number of data points. Quoted uncertainties on slope and intercept correspond to the 95% confidence limits.

Statistical parameters show that Eqn (8) is less precise than Eqn (9), indicating that the data obtained at higher pressure of the collision gas are more reliable. We checked that the results of Eqn (8) established for the same 28 compounds as for Eqn (9) are not significantly different from those reported above. To check the origin of the lower precision in Eqn (8), we correlated also the $\ln[I(B_1\text{Li}^+)/I(i\text{-PrCNLi}^+)]$ data determined at the two different pressures but treated in the same way. The most precise regression equation corresponds to the 'weighted mean' treatment:

$$\begin{aligned} \ln \left[\frac{I(B_1\text{Li}^+)}{I(i\text{-PrCNLi}^+)} \right]_{\text{low pressure}} &= (-0.030 \pm 0.220) \\ &+ (0.705 \pm 0.023) \ln \left[\frac{I(B_1\text{Li}^+)}{I(i\text{-PrCNLi}^+)} \right]_{\text{high pressure}} \quad (10) \\ r &= 0.9998, s = 0.24, n = 28. \end{aligned}$$

The high precision of Eqn (10) indicates that the lower precision of Eqn (8) is due to the less accurate 'intercept' data at low pressure. As mentioned above, this kind of extrapolation is rendered less accurate by the use of a range of higher energies. The values obtained at high pressure, using the 'weighted mean' treatment, were chosen as the most reliable set. The use of high pressure leads to a better signal-to-noise ratio and a better repeatability of individual measurements.

The precision of the correlations between the four

Table 1. Relative lithium cation basicities obtained using the kinetic method: upward extension of the scale to phosphoryl compounds

No.	B ₁ Formula	B ₂ ^d	ln[(B ₁ Li ⁺)/(i-PrCNLi ⁺)] ^a				
			Low pressure ^b Intercept ^e	Weighted mean ^f	B ₂ ^d	High pressure ^c Intercept ^e	Weighted mean ^f
1	<i>i</i> -PrCN		0.00	0.00		0.00	0.00
2	<i>t</i> -BuCN		0.75	0.69	1	1.33	1.01
3	Me ₂ SO ₂	2	1.99	1.82	2	3.04	2.70
4	<i>c</i> -PrCOMe	3	1.74	2.02	3	3.40	2.97
5	(PhO)MeSO ₂	2, 4	2.25 ± 0.25	2.07 ± 0.28			
6	<i>c</i> -Pr ₂ CO	5	3.53	3.34	4	5.19	4.93
7	(Ph)MeSO ₂	6	4.40	4.11			
8	HCONHMe	7	4.39	3.91			
9	MeCONH ₂	6, 7	4.93 ± 0.13	4.87 ± 0.01	6	6.82	6.55
10	(<i>p</i> -MePh)MeSO ₂	4	5.32	4.36			
11	Ph ₂ SO ₂	8	5.83	5.58	13	10.30	8.69
12	HCONMe ₂ (DMF)	11	6.08	6.17	11	10.01	8.72
13	MeCONHMe	9	6.72	6.40	9	9.44	8.74
14	Me ₂ SO (DMSO)	8, 10, 11, 12	6.90 ± 0.80	6.27 ± 0.58	11	10.53	9.62
15	(Ph)MeSO	12	7.78	7.66			
16	(MeO) ₂ HPO	12	7.82	7.42	12	12.86	10.76
17	MeCONME ₂ (DMA)	12, 14, 15, 16	8.21 ± 0.21	7.83 ± 0.41	11, 12, 14, 16	12.37 ± 0.48	10.90 ± 0.06
18	Ph ₂ SO	17	9.06	8.72 ± 0.05	17	13.78	12.14
19	(MeO) ₃ PO	16, 18	9.25 ± 0.05	9.18 ± 0.51	16, 18	14.98 ± 0.95	12.88 ± 0.11
20	(MeO) ₂ MePO	19	9.54	9.37	19	15.26	13.24
21	(ClCH ₂)(EtO) ₂ PO	19, 20	9.60 ± 0.30	9.34 ± 0.01	19, 20	15.72 ± 0.38	13.48 ± 0.01
22	(<i>i</i> -PrO) ₂ HPO	21	9.73	9.54	21	15.65	13.35
23	(MeO)MePhPO	19, 20	10.13 ± 0.14	10.41 ± 0.02	19, 20, 31	16.87 ± 0.27	14.92 ± 0.15
24	Me ₃ PO	23	10.14	10.76	23, 25	17.73 ± 0.16	15.80 ± 0.14
25	(EtO) ₃ PO	20, 23, 24	10.37 ± 0.42	10.86 ± 0.41	19, 20, 23	17.17 ± 0.26	14.88 ± 0.10
26	(<i>p</i> -CF ₃ PhO)(Ph) ₂ PO	20	10.60	9.51	20	16.32	13.65
27	(<i>p</i> -FPhO)(Ph) ₂ PO	24, 25	10.87 ± 0.06	11.04 ± 0.38	24, 25	18.15 ± 0.73	15.49 ± 0.18
28	(PhO) ₃ PO	26	11.06	11.01	25	17.35	15.03
29	Et ₃ PO	24	11.52	12.00	24	19.86	17.40
30	(PhO)Ph ₂ PO	24, 29	11.82 ± 0.17	12.28 ± 0.10	24, 29	20.63 ± 0.61	17.69 ± 0.01
31	(EtO) ₂ MePO	23, 26	11.90 ± 0.35	10.46 ± 0.48	26	16.45	14.70
32	(Me ₂ N) ₃ PO (HMPA)	29	12.80	12.94	29	20.99	18.56
33	Ph ₃ PO	29, 32	12.85 ± 0.01	12.99 ± 0.18	29, 32	21.04 ± 0.02	18.60 ± 0.01

^a Values relative to *i*-PrCN are obtained by summing individual ln[(B₁Li⁺)/(B₂Li⁺)] values. When indicated, uncertainty is the standard deviation of the mean value obtained from several reference compounds B₂.

^b Total pressure: 1.0 × 10⁻⁴ Pa.

^c Total pressure 5.0 × 10⁻⁴ Pa.

^d Compounds used as references in individual measurements; same numbering as in column B₁.

^e From extrapolation of individual ln[(B₁Li⁺)/(B₂Li⁺)] to zero kinetic energy.

^f From the weighted mean of individual ln[(B₁Li⁺)/(B₂Li⁺)].

sets of data, obtained under different experimental conditions, using two different data treatments, may be used as a probe of the reliability of the method. In the worst case, Eqn (8), the standard deviation on ln[I(B₁Li⁺)/I(*i*-PrCNLi⁺)] values is 0.44. Considering the more precise Eqns (9) and (10), we estimate that the mean precision of the method lies between 0.2 and 0.5 ln[I(B₁Li⁺)/I(*i*-PrCNLi⁺)] units. This may be translated into energy units after calibration (see below).

The values of ln[I(B₁Li⁺)/I(*i*-PrCNLi⁺)] obtained at high pressure, using the 'weighted mean' treatment, were correlated with *LCB* values (in kJ mol⁻¹) determined in Taft's laboratory^{4f} using the equilibrium method at the nominal working temperature of 373 K:

$$\ln[I(B_1Li^+)/I(i-PrCNLi^+)] = (0.246 \pm 0.610) + (0.372 \pm 0.028)\Delta LCB \quad (11)$$

$$r = 0.9965, s = 0.45, n = 9.$$

As can be seen in Fig. 1, the points corresponding to dimethyl sulfoxide (DMSO) and *N*-methylacetamide deviate significantly from the observed linear trend and were excluded from the regression treatment, leading to Eqn (11). Noteworthily, inclusion of points for DMSO and *N*-methylacetamide in the regression equation does not change its parameters significantly (intercept = 0.569; slope = 0.375). The deviation of DMSO was already observed in previous work,^{8a} and attributed to the rapid formation of homo- and heterodimers during the equilibrium experiments.^{4f} Concerning *N*-methylacetamide, we noticed that its *LCB* does not fit the trend of *N*-methyl substitution effects on H⁺ and Li⁺ basicities in the amide series, as seen in Table 2.

From the slope in Eqn (11), we obtained an 'effective temperature' $T_{\text{eff}} = 323 \pm 24$ K of excited Li⁺-bonded dimers at a nominal pressure of 5 × 10⁻⁴ Pa. By com-

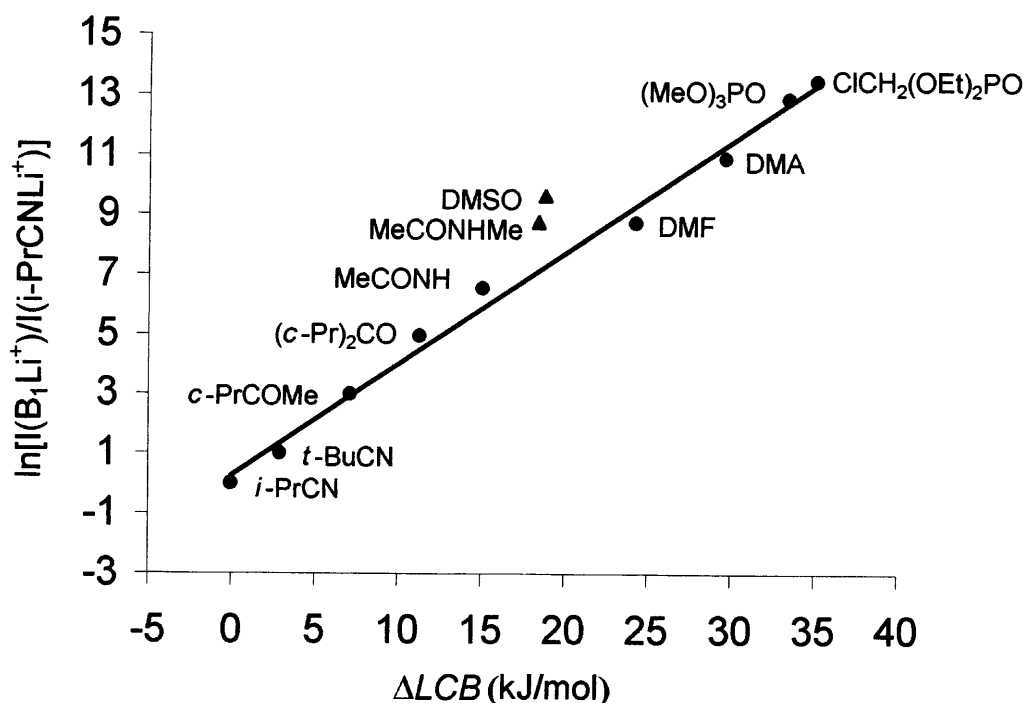


Figure 1. Lithium cation basicities in the form of $\ln[(B_1Li^+)/I(i-PrCNLi^+)]$ vs. ΔLCB relative to *i*-PrCN. Values of ΔLCB from Ref. 4f. DMSO and MeCONHMe excluded from the least-squares treatment (see text).

binning the slopes in Eqns (10) and (11) we obtained $T_{\text{eff}} = 455 \pm 35$ K for the excited dimers at a nominal pressure of 1×10^{-4} Pa. It was pointed out that this effective temperature is in fact a qualitative indication of the degree of excitation of the fragmenting heterodimer.⁷ This means that in our experiments the dimer activated at higher pressure is less excited than at low pressure. Our experimental conditions clearly correspond to a multiple collision regime, as seen from the number of collisions evaluated according to Hop *et al.*¹³ For example, for a collision time of 12.5 ms the ion $[(CH_3O)_3PO]_2Li^+$ suffers about four and 20 collisions at pressures of 1.0×10^{-4} Pa and 5.0×10^{-4} Pa, respectively. We do not exclude that a small fraction of ions collide, and eventually dissociate, during the excitation period, which is 125 μ s in this example.

Table 2. *N*-Methylation effects on proton and lithium cation basicities in the amide series

Compound	ΔGB^b	ΔLCB^b
HCONH ₂	0.0	0.0
HCONHMe	29.1	13.4
HCONMe ₂	64.0 (34.9)	21.4 (8.0)
MeCONH ₂	0.0	0.0
MeCONHMe	25.0	3.2
MeCONMe ₂	44.4 (19.4)	14.5 (11.3)

^a kJ/mol⁻¹, data obtained using the equilibrium method; *GBs* from Ref. 22d; *LCBs* from Ref. 4f.

^b Effect of the second *N*-methylation is given in parentheses.

It appears that dissociations corresponding to a larger number of collisions occur at a lower internal energy. Probably, the ions gain enough energy to be dissociated by a stepwise process, which resembles the SORI (sustained off-resonance irradiation)¹⁴ excitation, a typical low-energy method. In fact, we have carried out SORI experiments for a few systems, observing a great similarity both in the ratios $I(B_1Li^+)/I(B_2Li^+)$ and in the range of $E_{k,cm}$ used for the dissociation of the heterodimer. We noticed that the collision energy $E_{k,cm}$ imparted initially to ions, necessary for dissociating significantly some phosphoryl heterodimers at low pressure, exceeds by ~ 7 eV the energy necessary at high pressure. We also observed that the repeatability of the measures obtained at higher pressure was better than that observed for the experiments carried out at low pressure. In other words, the abundance of B_1Li^+ ions and the signal-to-noise ratio were larger in the former case. Experimentally, it is known that, as the internal energy of ion increases, the abundances of the fragments originating from proton-bonded dimers become closer.¹⁵ For all the experiments carried out at low and high pressures, the ratio $I(B_1Li^+)/I(B_2Li^+)$ is larger for the latter conditions, indicating a corresponding lower internal energy of the dimer ion excited at high pressure.

Scale of lithium cation basicity for phosphoryl compounds

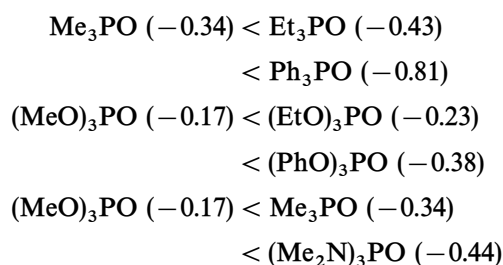
In Fig. 2, we present a ladder of ΔLCB values for 16 organophosphorus compounds, covering a range of 21 kJ mol⁻¹. The reported values are referenced to the

equilibrium scale^{4f} established at 373 K. These compounds, with the general structure $R_1R_2R_3PO$, can be sorted into five groups: phosphine oxides ($R_1, R_2, R_3 = \text{alkyl, aryl}$), phosphinates ($R_1, R_2 = \text{alkyl, aryl}$ and $R_3 = \text{alkoxy, phenoxy}$), phosphonates ($R_1 = \text{alkyl, aryl}$ and $R_2, R_3 = \text{alkoxy, phenoxy}$), phosphates ($R_1, R_2, R_3 = \text{alkoxy, phenoxy}$) and hexamethylphosphoramide (HMPA, $R_1, R_2, R_3 = \text{dimethylamino}$). We used the weakest phosphoryl base, $(\text{MeO})_2\text{HPO}$, as the anchor point for the scale in Fig. 2.

Except for the experiments involving $(\text{MeO})_2\text{HPO}$ and $(\text{MeO})_3\text{PO}$, the *LCBs* were determined using only phosphoryl derivatives as reference bases. We chose a homogeneous family of compounds with the aim of minimizing entropic effects¹⁶ in the measurement of *LCBs* by the kinetic method. Anyway, it should be noted that entropic effects could not be totally eliminated, and this would certainly be one of the major limitations in the application of the kinetic method. In addition, as this range of high *LCBs* has not been explored before, we could not determine the *LCB* values for the phosphoryl compounds using the kinetic method in its conventional form.⁷ Following this methodology, *LCB* values for a compound B_1 could be determined from a calibration line corresponding to the regression of $\ln[I(B_1\text{Li}^+)/I(B_2\text{Li}^+)]$ values (obtained by opposing successively the compound B_1 under scrutiny to a series of reference compounds B_2 belonging to a homogeneous family) against the *LCB* values of the reference compounds B_2 . From this line, both the *LCB* of B_1 and T_{eff} could be calculated. In this work, the ΔLCB values for the phosphoryl derivatives (Fig. 2) were obtained using the model Eqn (7b), combining $T_{\text{eff}} = 323$ K (not significantly lower than the temperature of the FT-ICR cell, 338 K) calculated from the calibration Eqn (11), and the $\ln[I(B_1\text{Li}^+)/I(i\text{-PrCNLi}^+)]$ values obtained under the same conditions as for the data used to establish the calibration Eqn (11). From the estimated precision in $\ln[I(B_1\text{Li}^+)/I(i\text{-PrCNLi}^+)]$ units, stated above, a precision of 0.5–1.3 kJ mol^{-1} on the relative *LCBs* is calculated. All the derivatives, except nitrile compounds, used to establish the calibration line are oxygen bases of general structures $R_1R_2\text{CO}$, $R_1R_2\text{SO}$, $R_1R_2\text{SO}_2$ and $R_1R_2R_3\text{PO}$. The bonding to Li^+ in the dimers formed with these compounds is not expected to be altered by steric effects, the bulky substituents being remote from the reactive center. $R_1R_2\text{CO}$, $R_1R_2\text{SO}$ and $R_1R_2R_3\text{PO}$ derivatives are likely to bond Li^+ as monodentate ligands. The case of $R_1R_2\text{SO}_2$ compounds, which are potential bidentate ligands, has been examined in a recent paper,^{8b} where it was concluded that the sulfonyl group is not likely to form a bidentate adduct with Li^+ . The similar behavior of all these compounds is reflected in the goodness of fit of Eqn (11). We postulate that the newly studied phosphoryl compounds behave similarly to the set of compounds used in establishing the calibration line. This is the reason for which we used the T_{eff} inferred from Eqn (11) to obtain ΔLCBs for phosphoryl compounds. In this way we have extended upward the *LCB* scale^{4f} by about 14 kJ mol^{-1} . Currently, the $\text{P}=\text{O}$ compounds studied here are the monofunctional ligands with the highest *LCB* values yet reported.

Taft and Topsom proposed a general treatment of the

substituent effects on proton-transfer equilibria,¹⁷ later extended to other cation affinities.^{4f} Substituent effects were separated into field, resonance and polarizability components, and quantitatively described by the substituent constants σ_F , σ_R and σ_α , respectively. Abboud *et al.*¹⁸ successfully correlated the *LCAs* of alcohols and ethers with the polarizability parameter. This treatment is not possible within the series of phosphoryl compounds studied here, because we cannot select families of derivatives in which the substituents could be varied one at a time within a range of effects sufficiently large to be significant. A treatment using the sum of substituent σ constants, assuming additivity, did not lead to a meaningful correlation. Nevertheless, from the following *LCB* sequences, it appears that the substituent effect follows roughly the order of polarizability, expressed by σ_α (given in parentheses; note that an increase in polarizability corresponds to a more negative value):¹⁷



The *LCB* increasing effect of the substituent linked to the phenyl ring in the diphenylphosphinate series, $\text{CF}_3 < \text{F} < \text{H}$, follows the σ_p^- or σ_p^0 order (the subscript p represents the *para* position; the superscripts minus and zero represent an electron-rich system and a system with minimal resonance interaction, respectively),¹⁹ but a precise proportionality is not observed. Mastryukova and Kabachnik²⁰ proposed the Hammett-like substituent constant σ^{ph} , specially designed for the description of acid–base properties of phosphorus compounds. Usually, these constants are used as a sum $\Sigma\sigma^{\text{ph}}$. Again, we did not find significant relationships. Although Bollinger and co-workers²¹ claimed the existence of a correlation between *GB* (gas basicity, Gibbs energy of proton transfer) and σ^{ph} , examination of their results shows that the only phosphate ester included deviates badly. Clearly, the σ^{ph} are not suited for the description of substituent effects in the gas phase.

Chelation of Li^+ by bidentate nitrogen ligands^{4h} or by polydentate oxygen ligands^{4a,4r} strongly enhances the observed basicity as compared with the equivalent monodentate ligand. This kind of effect is not apparent in the phosphoryl compounds bearing alkoxy groups, and chelation of Li^+ by the compounds investigated in this work is likely not to occur. The hypothesis of chelation has been rejected previously on the basis of PM3 calculations.^{5j} Interestingly, *ab initio* calculations on the interaction between the anion $(\text{HO})_2\text{PO}_2^-$ and Li^+ show that the chelated structure is unfavorable.^{5s} An empirical confirmation could be obtained by a comparison between *GB* and *LCB* values⁸ for these compounds. Unfortunately, using the *GBs* currently available,^{6,21,22} we were not able to obtain a meaningful correlation. Before drawing conclusions from this lack of fit we plan a new determination of these *GBs*.

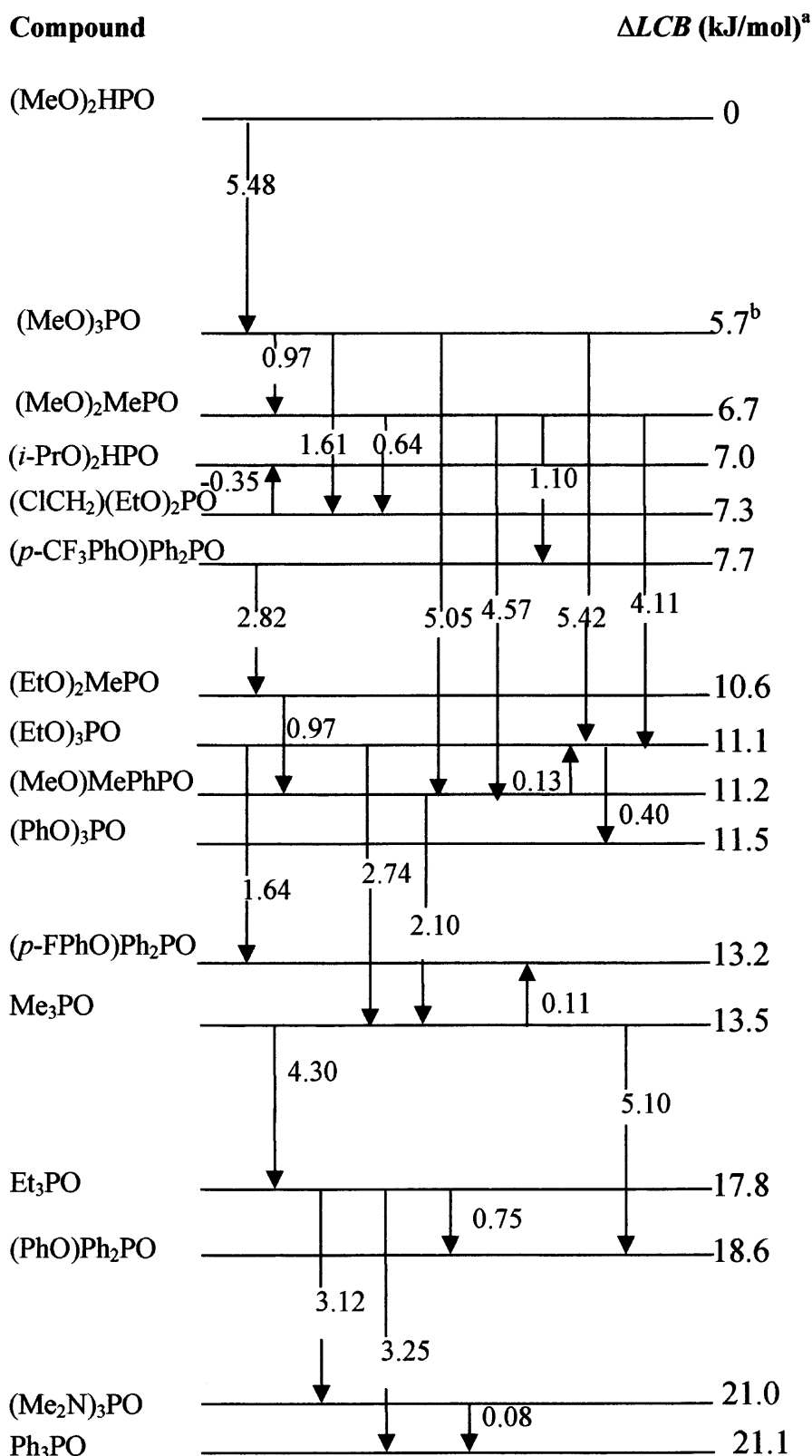


Figure 2. Lithium cation basicities of phosphoryl compounds. ΔLCB values referred to (MeO)₂HPO. ^a ΔLCB values correspond to increments resulting from one or several experimental steps (arrows are drawn from the compound used as reference to the compound to be determined; a positive value corresponds to a newly determined compound more basic than the reference compound), uncertainties on these data are estimated to fall in the range 0.5–1.3 kJ mol⁻¹ (see text). ^b This value takes into account other experiments involving non-phosphoryl compounds (see Table 1).

CONCLUSION

The effect of increasing the pressure of the collision gas used for the measurement of *LCB* by the kinetic method⁷ was examined for a series of compounds (nitrile, carbonyl, sulfonyl and phosphoryl derivatives), the *LCBs* of which spans a range of 35 kJ mol⁻¹. We showed that a fivefold increase in the collision-gas pressure permits one to decrease the initial kinetic energy imparted to the lithium-bonded dimer for obtaining a significant dissociation and to increase the efficiency of the dissociation process. The relative *LCBs* obtained by the kinetic method were calibrated against *LCB* values based on equilibrium measurements. The effective temperature determined from this calibration was used to establish *LCBs* for a series of phosphoryl compounds. We found that these derivatives have the largest *LCBs* in the current basicity scale, which was extended upward by 14 kJ mol⁻¹ during this work. However, this part of the scale constitutes an extrapolation of the Taft *LCB* scale, and the newly determined values are more

prone to systematic error than interpolated values usually obtained by the classical kinetic method. It should be also pointed out that entropy effects are not taken into account within the approximations involved in the derivation of Eqn (7b).

From an analytical point of view, selective Li⁺ cationization of phosphoryl derivatives can be envisioned. This could be a powerful tool for the detection and quantitation of compounds with similar functionalities well known for their toxicity, such as nerve agents²³ and their possible simulants,²⁴ precursors²⁵ or degradation products,²⁶ pesticides²⁷ and related compounds²⁸ and flame retardants.²⁹

Acknowledgements

The work of A.C. and M.H. at UNSA was supported by NATO (grant No. CRG 931176) and the Spanish Ministry of Education (Dirección General de Enseñanza), respectively. The work of S.A.F. at UNSA was carried out under ERASMUS European exchange program.

REFERENCES

- (a) K. Eller and H. Schwarz, *Chem. Rev.* **91**, 1121 (1991); (b) K. Eller, *Coord. Chem. Rev.* **126**, 93 (1993); (c) D. Schröder and H. Schwarz, *Angew. Chem., Int. Ed. Engl.* **34**, 1973 (1995); (d) A.-M. Sapse and P. v. R. Schleyer, Eds *Lithium Chemistry: a Theoretical and Experimental Overview*. Wiley, New York (1995); (e) B. S. Freiser, *J. Mass Spectrom.* **31**, 703 (1996); (f), M. J. Pregel, E. J. Dunn, R. Nagelkerke, G. R. J. Thatcher and E. Bunzel, *Chem. Soc. Rev.* **24**, 449 (1995).
- (a) C. J. Pedersen, *J. Am. Chem. Soc.* **89**, 7017 (1967); (b) I. Sutherland, *Chem. Soc. Rev.* **15**, 63 (1986); (c) E. J. Dunn and E. Bunzel, *Can. J. Chem.* **67**, 1440 (1989); (d) E. J. Dunn, R. Y. Moir, E. Bunzel, J. G. Purdon and R. A. B. Bannard, *Can. J. Chem.* **68**, 1837 (1990); (e) E. Bunzel, E. J. Dunn, Ng. Truong, R. A. B. Bannard and J. G. Purdon, *Tetrahedron Lett.* **31**, 6513 (1990); (f) D. A. Dougherty, *Science* **271**, 163 (1996); (g) J. C. Ma and D. A. Dougherty, *Chem. Rev.* **97**, 11303 (1997).
- (a) L. M. Teesch and J. Adams, *J. Am. Chem. Soc.* **113**, 812 (1991); (b) L. M. Teesch and J. Adams, Chap. 2, *Experimental Mass Spectrometry*, edited by D. H. Russell. Plenum Press, New York (1994); (c) M. Takayama, T. Fukai, T. Nomura and T. Yamauchi, *Org. Mass Spectrom.* **26**, 655 (1991); (d) M. Takayama, *Org. Mass Spectrom.* **28**, 878 (1993); (e) M. Takayama, *Int. J. Mass Spectrom. Ion Processes* **136**, 35 (1994); (f) T. Fujii, *Chem. Phys. Lett.* **191**, 162 (1992); (g) L. C. Ngoka, J.-F. Gal and C. Lebrilla, *Anal. Chem.* **66**, 692 (1994); (h) M. T. Rodgers, S. A. Campbell and J. L. Beauchamp, *Int. J. Mass Spectrom. Ion Processes* **161**, 193 (1997); (i) M. R. Asam and G. L. Glish, *J. Am. Soc. Mass Spectrom.* **8**, 957 (1997).
- (a) S. K. Searles and P. Kebarle, *Can. J. Chem.* **47**, 2619 (1969); (b) I. Dzidic and P. Kebarle, *J. Phys. Chem.* **74**, 1466 (1970); (c) P. Kebarle, *Annu. Rev. Phys. Chem.* **28**, 445 (1977); (d) R. H. Staley and J. L. Beauchamp, *J. Am. Chem. Soc.* **97**, 5920 (1975); (e) R. L. Woodin and J. L. Beauchamp, *J. Am. Chem. Soc.* **100**, 501 (1977); (f) R. W. Taft, F. Anvia, J.-F. Gal, S. Walsh, M. Capon, M. C. Holmes, K. Hosn, O. Oloumi, R. Vasanwala and S. Yazdani, *Pure Appl. Chem.* **62**, 17 (1990); (g) M. Alcamí, O. Mó, M. Yáñez, F. Anvia and R. W. Taft, *J. Phys. Chem.* **94**, 4796 (1990); (h) F. Anvia, S. Walsh, M. Capon, I. A. Koppel, R. W. Taft, J. L. G. de Paz and J. Catalán, *J. Am. Chem. Soc.* **112**, 5095 (1990); (i) S. Maleknia and J. Brodbelt, *J. Am. Chem. Soc.* **114**, 4295 (1992); (j) C.-C. Liou and J. S. Brodbelt, *J. Am. Soc. Mass Spectrom.* **3**, 543 (1992); (k) H. I. Chu and D. V. Dearden, *J. Am. Chem. Soc.* **117**, 8197 (1995); (l) S. Lee, T. Wyttenbach, G. von Helden and M. T. Bowers, *J. Am. Chem. Soc.* **117**, 10159 (1995); (m) B. A. Cerda and C. Wesdemiotis, *J. Am. Chem. Soc.* **117**, 9734 (1995); (n) V. T. Borret, R. Colton and J. C. Traeger, *Eur. Mass Spectrom.* **1**, 131 (1995); (o) E. A. Steel, K. M. Merz and A. W. Castleman, *J. Phys. Chem.* **99**, 7829 (1995); (p) Q. Chen, K. Cannell, J. Nicoll and D. V. Dearden, *J. Am. Chem. Soc.* **118**, 6335 (1996); (q) M. B. More, E. D. Glendening, D. Ray, D. Feller and P. B. Armentrout, *J. Phys. Chem.* **100**, 1605 (1996); (r) D. Ray, D. Feller, M. B. More, E. D. Glendening and P. B. Armentrout, *J. Phys. Chem.* **100**, 16166 (1996); (s) M. T. Rodgers and P. B. Armentrout, *J. Phys. Chem.* **101**, 1238 (1997); (t) M. T. Rodgers and P. B. Armentrout, *J. Phys. Chem.* **101**, 2614 (1997); (u) M. T. Cancilla, S. G. Penn, J. A. Carroll and C. Lebrilla, *J. Am. Chem. Soc.* **118**, 6736 (1996).
- (a) S. F. Smith, J. Chandrasekhar and W. L. Jorgensen, *J. Phys. Chem.* **86**, 3308 (1982); (b) J. E. Del Bene, M. J. Frisch, K. Raghavachari and J. A. Pople, *J. Phys. Chem.* **86**, 1529 (1982); (c) J. E. Del Bene, *J. Phys. Chem.* **88**, 5927 (1984); (d) A. M. Sapse, J. D. Bunce and D. C. Jain, *J. Am. Chem. Soc.* **106**, 6579 (1984); (e) M. Alcamí, O. Mó and M. Yáñez, *J. Phys. Chem.* **93**, 3929 (1989); (f) M. Alcamí, O. Mó, J. L. G. de Paz and M. Yáñez, *Theor. Chim. Acta*, **77**, 1 (1990); (g) R. S. Alexander, Z. F. Kanyo, L. E. Chirlian and D. Christianson, *J. Am. Chem. Soc.* **112**, 933 (1990); (h) F. Jensen, *J. Am. Chem. Soc.* **114**, 9533 (1992); (i) E. D. Glendening, D. Feller and M. A. Thompson, *J. Am. Chem. Soc.* **116**, 10657 (1994); (j) J.-F. Gal, I. Koppel, R. Kurg and P.-C. Maria, *Int. J. Quantum Chem.* **59**, 409 (1996); (k) E. Nakamura, S. Mori and K. Morokuma, *J. Am. Chem. Soc.* **119**, 4900 (1997).
- R. V. Hodges, T. J. McDonnell and J. L. Beauchamp, *J. Am. Chem. Soc.* **102**, 1327 (1980).
- R. G. Cooks, J. S. Patrick, T. Kotiaho and S. A. McLuckey, *Mass Spectrom. Rev.* **13**, 287 (1994).

8. (a) E. Buncel, M. Decouzon, A. Formento, J.-F. Gal, M. Herberos, L. Li, P.-C. Maria, I. Koppel and R. Kurg, *J. Am. Soc. Mass Spectrom.* **8**, 262 (1997); (b) A. M. P. Borrajo, J.-F. Gal, P.-C. Maria, M. Decouzon, D. C. Ripley, E. Buncel and G. R. J. Thatcher, *J. Org. Chem.* **62**, 9203 (1997).
9. S. Hoz, E. J. Dunn, E. Buncel, R. A. B. Bannard and J. G. Purdon, *Phosphorus Sulfur* **24**, 321 (1985).
10. M. Decouzon, J.-F. Gal, S. Géribaldi, P.-C. Maria and M. Rouillard, *Spectra 2000* **17**, 51 (1989).
11. L. C. Zeller, J. T. Farrell, H. I. Kenttämäa and T. Kuivalainen, *J. Am. Soc. Mass Spectrom.* **4**, 125 (1993).
12. S. P. Craig, M. Zhong, B. Choo and J. I. Brauman, *J. Phys. Chem. A*, **101**, 19 (1997).
13. (a) C. E. C. A. Hop, T. B. McMahon and G. D. Willett, *Int. J. Mass Spectrom. Ion Processes* **101**, 191 (1990); equation given in a previous paper, corrected in C. E. C. A. Hop, McMahon, *J. Phys. Chem.* **95**, 10582 (1991).
14. (a) J. W. Gauthier, T. R. Trautman, D. B. Jacobson, *Anal. Chim. Acta* **246**, 211 (1991); (b) S. A. McLuckey and D. E. Goeringer *J. Mass Spectrom.* **32**, 461 (1997).
15. S. T. Gaul, M. E. Schnute and R. R. Squires, *Int. J. Mass Spectrom. Ion Processes* **96**, 181 (1990).
16. X. Cheng, Z. Wu and C. Fenselau, *J. Am. Chem. Soc.* **115**, 4844 (1993).
17. R. W. Taft and R. D. Topsom, *Prog. Phys. Org. Chem.* **16**, 1 (1987).
18. J.-L. M. Abboud, M. Yáñez, J. Elguero, D. Liotard, M. Essefar, M. El Mouhtadi and R. W. Taft, *New J. Chem.* **16**, 739 (1992).
19. O. Exner, *Correlation Analysis of Chemical Data*. Plenum Press, New York (1988).
20. T. A. Mastryukova and M. I. Kabachnik, *Russ. Chem. Rev.* **38**, 795 (1969).
21. (a) J. C. Bollinger, R. Houriet and T. Yvernault, *Phosphorus Sulfur* **19**, 379 (1984); (b) J. C. Bollinger, R. Houriet, C. W. Kern, D. Perret, J. Weber and T. Yvernault, *J. Am. Chem. Soc.* **107**, 5352 (1985).
22. (a) S. G. Lias, J. F. Liebman and R. D. Levin, *J. Phys. Chem. Ref. Data* **13**, 695 (1984); (b) S. G. Lias, J. E. Bartmess, J. F. Liebman, J. L. Holmes, R. D. Levin and W. G. Mallard, *J. Phys. Chem. Ref. Data* **17**, Suppl. 1 (1988); (c) *NIST Positive Ion Energetics Database, Version 1.1*, NIST Standard Reference Database 19A. NIST, Gaithersburg, MD (1990); (d) E. P. Hunter and S. G. Lias, *J. Phys. Chem. Ref. Data* submitted for publication.
23. *Conference on Disarmament, The Convention on the Prohibition of the Development, Production, Stockpiling and Use of Chemical Weapons and on their Destruction*, United Nations Document CD/1170. United Nations, Geneva (1992); (b) R. J. Mathews and T. L. H. McCormack, *Security Dialogue* **26**, 93 (1995).
24. M. W. Buchanan, R. L. Hettich, J. H. Xu, L. C. Waters and A. Watson, *J. Hazard. Mater.* **42**, 49 (1995).
25. M. W. Wensing, A. P. Snyder and C. S. Harden, *Rapid Commun. Mass Spectrom.* **10**, 1259 (1996).
26. V. T. Borret, R. J. Mathews, R. Colton and J. C. Traeger, *Rapid Commun. Mass Spectrom.* **10**, 114 (1996).
27. (a) G. Durán, F. Sánchez-Baeza, A. Messeguer and D. Barceló, *Biol. Mass Spectrom.* **20**, 3 (1991); (b) S. Lacorte, C. Molina and D. Barceló, *Anal. Chim. Acta* **281**, 71 (1993); (c) S. Lacorte and D. Barceló, *J. Chromatogr. A* **712**, 103 (1995).
28. S. Onodera, S. Maeda and T. Saitoh, *Kankyo Kagaku (J. Environment. Chem.)* **5**, 617 (1995).
29. T. Hudec, J. Thean, D. Kuehl and R. C. Dougherty, *Science* **211**, 951 (1981).