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THE APPLICATION OF THE SIMPLIFIED FORM OF THE QUASI-EQUILIBRIUM THEORY TO THE MASS SPECTRA OF SOME MONONUCLEAR METAL CARBONYLS

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Summary

The concept of molecular ions and metal-containing fragment ions formed in the mass spectra of the mononuclear metal carbonyls, $M(CO)_6$ (M = Cr, Mo,W), $Fe(CO)_5$, $Ni(CO)_4$, containing the metal in an excited state appears to violate the quasi-equilibrium theory. Calculations, using the simplified form of the theory, show that the high values obtained for the heats of formation of the metal ions determined by mass spectrometry are consistent with the "excess energies" representing kinetic shifts.

A number of studies [1] have been reported in which thermochemical data for metal carbonyls has been obtained by mass spectrometric means. These have included the evaluation of bond dissociation energies and heats of formation of both molecular and fragment ions. It is notable that the values of heats of formation of the metal ions (M^{+}) determined by such methods exceed those determined by spectroscopic methods. In the initial studies of the mononuclear metal carbonyls $M(CO)_6$ (M = Cr, Mo,W), $Fe(CO)_5$ and $Ni(CO)_4$, Winters and Kiser [2,3] suggested that this "excess energy" in mass spectrometrically determined heats of formation were consistent with the metal ions being formed in valence excited states and these authors found a good correlation between the "excess energy" and the metal ion excitation energy in all cases except for $Ni(CO)_4$. More recent work by Junk and Svec [4] essentially substantiates the results of Winters and Kiser, although there are small differences in the actual numerical values obtained. These authors also suggest that M^{+} ions are formed in excited states. Given in Table 1 are the values for $\Delta H_f(M^{+})$ reported by both groups and these are compared with the spectroscopically determined values.

TABLE 1

COMPARISON OF ΔH_f ($M^{\ddagger}$) DETERMINED BY MASS SPECTRAL AND SPECTROSCOPIC MEANS

Ion	Source	ΔH_f (mass spec.)[a,b]	ΔH_f (spectroscopic)[a]
Ni^+	$Ni(CO)_4$	1325 (1379)	1167
Fe^+	$Fe(CO)_5$	1363 (1379)	1180
Cr^+	$Cr(CO)_6$	1300 (1363)	1050
Mo^+	$Mo(CO)_6$	1635 (1743)	1343
W^+	$W(CO)_6$	1927 (1994)	1618

[a] Values quoted in kJ mole^{-1} [b] Values taken from ref. 4, figures in parentheses from refs. 2 and 3.

It is now well established that the electron removed in the ionisation process for the mononuclear carbonyls listed above, is of principally metallic character [1] and the results quoted above indicate that ionisation leaves the metal atom of the molecular ion of each complex in an excited state. Furthermore, the metal remains in the excited state throughout the full sequence of mass spectral fragmentations. Such a situation raises serious problems in terms of currently accepted models of mass spectral behaviour. That is, these systems appear to be in opposition to one of the fundamental assumptions of the quasi-equilibrium theory (QET) [5] namely, that initial excitation energy randomises throughout the molecule at a rate which is fast relative to bond dissociation. However, there is an alternative explanation for these differences in heats of formation and that is, that the internal energy of the molecular ion is partitioned between the available oscillators and the discrepancy arises as a consequence of loss of internal energy to the carbon monoxide molecules eliminated in successive decompositions. Since the probability of imparting no internal energy to the CO molecules would intuitively appear to be essentially negligable, the "excess energy" therefore represents energy required to produce measurable quantities of $M^{\ddagger}$ ions from $M(CO)_n{}^{\ddagger}$ at a rate that is appropriate to the mass spectrometric time scale. The "excess energy" is thus what is more often referred to as the kinetic shift*.

It is the purpose of this paper to discuss such energy partitioning in terms of the simplified form of the QET, the basic equation for which is:

$$k = \nu \left(\frac{E - E_0}{E}\right)^{s-1} \qquad (1)$$

where k is the rate constant for the reaction in question, ν is a frequency factor that for single bond cleavage reactions may be taken as the vibrational frequency of the bond in question, E is the total internal energy of the molecular ion and E_0 is the activation energy for the process under consideration. The symbol s, is defined as the number of effective oscillators (i.e. the number of vibrational modes; $3n - 6$ for an n atom polyatomic molecule). Previous studies on organic molecules have shown that s should be treated as the number of effec-

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* The kinetic shift is defined as the excess energy, above the true activation energy for the reaction, that is necessary in order to make the reaction proceed at a rate appropriate to the mass spectroscopic time scale. For a detailed discussion, see ref. 6.

tive oscillators and in practice, values varying from one-half to one-fifth of the total have been found appropriate at energies close to the threshold.

Previous studies of the fragmentation of metal carbonyls have shown that the main route of decomposition of such molecules is by a sequential loss of CO ligands, viz.:

$$(M(CO)_n^{+\cdot} \rightarrow M(CO)_{n-1}^{+\cdot} \rightarrow M(CO)_{n-2}^{+\cdot} \rightarrow \ldots\ldots \rightarrow M(CO)^{+\cdot} \rightarrow M^{+\cdot} \qquad (2)$$

Although, in a few cases, it has been reported that the molecular ion may lose more than one carbonyl group in a single step [1], it would seem intuitively unlikely that such a process would occur at energies close to the threshold and as it is such energies that are being considered here, the present discussion assumes the sequential decomposition mode to be adopted and that there is no other decomposition of the molecular ion that is able to compete with loss of a single CO molecule. On this basis it is possible to apply the simplified form of the QET to the first step of the sequential decomposition 2. That is, to examine the fraction of molecular ions undergoing the reaction:

$$M(CO)_n^{+\cdot} \rightarrow M(CO)_{n-1}^{+\cdot} + CO \qquad (3)$$

but having sufficient internal energy to undergo the full sequence of decompositions leading ultimately to $M^{+\cdot}$.

The question therefore arises as to the choice of suitable parameters of eqn. 1 for a molecular ion as described above. It is possible to estimate the minimum value of the internal energy of the molecular ion in the following way: the eqn. 4 can be treated as a summation of eqns. 5-7 in order to calculate the minimum internal energy required for a molecular ion to produce $M^{+\cdot}$ ions.

$$\underline{M(CO)_n^{+\cdot} \rightarrow M^{+\cdot} + nCO} \qquad (4)$$

$$M(CO)_n \rightarrow M + nCO \qquad \Delta H_r = n\bar{D}_o \qquad (5)$$

$$M \rightarrow M^{+\cdot} \qquad \Delta H_r = I_m \qquad (6)$$

$$M(CO)_n^{+\cdot} \rightarrow M(CO)_n \qquad \Delta H_r = -I_c \qquad (7)$$

Thus the minimum internal energy of $M(CO)_n^{+\cdot}$ ions fragmenting to $M^{+\cdot}$ ions is $n\bar{D}_o + I_m - I_c$ ($\bar{D}_o$ = mean metal—carbonyl bond dissociation energy; I_m = ionisation potential of the metal atom; I_c = ionisation potential of the complex). However, the experimental value of the internal energy of such molecular ions will be the minimum value plus the kinetic shift. The activation energy for process 3 is equal to the ionic bond dissociation energy for the loss of the first CO molecule (D_i). This can be evaluated from the difference between the appearance potential of the ion, $M(CO)_{n-1}^{+\cdot}$ and the ionisation potential of the complex (I_c)*. The value of the totally symmetric M—C stretching mode of each carbonyl has been taken as the frequency factor (ν), but the choice of an ap-

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* In deriving values for E and E_0, the thermochemical parameters have been chosen in such a way as to eliminate the use of data obtained for mass spectrometry. Thus, $\bar{D}_0$ can be obtained from thermochemical studies, and I_c from photo-electron spectroscopy. However to calculate D_i, the appearance potential of the daughter ion is required and this may itself be subject to a kinetic shift. Thus D_i values quoted may themselves be upper limits to the true values. Nevertheless, the error in E_0 will not significantly effect the results of the following treatment.

TABLE 2

RATE CONSTANTS AND THERMOCHEMICAL DATA FOR THE REACTION $M(CO)_n^{+\cdot} \rightarrow M(CO)_{n-1}^{+\cdot} + CO$[a]

Complex	I_m	$n\bar{D}_o$	I_c	E_{ex}	E	E_o	$(s-1)$	$\log \nu$[b]	$\log k$[c]
$Ni(CO)_4$	735	578	798	158	673	58	20	13.057	12.28 (12.79)
$Fe(CO)_5$	758	578	766	183	753	77	26	13.093	11.88 (12.00)
$Cr(CO)_6$	651	604	774	250	821	87	32	13.068	11.51 (12.40)
$Mo(CO)_6$	684	925	783	292	1118	77	32	13.079	12.08 (12.56)
$W(CO)_6$	769	1040	788	309	1330	77	32	13.111	12.28 (12.62)

[a] Data is presented for the molecular ions as defined in text undergoing reaction 3. All thermochemical data is taken from ref. 4 and the references cited therein, and is in kJmole^{-1}. The symbols, I_m, $\bar{D}_o$, I_c, E and E_o are defined in the text, E_{ex} is the excess energy. [b] The frequency factors were taken from ref. 8. [c] Log k values given in parentheses were calculated, using the "sliding-scale" method of evaluating the effective number of oscillators as discussed in the text.

propriate value for s is more difficult. The results given in Table 2 are for $s = 3n - 6$, however a lower value may be more appropriate near the threshold. The implications of such a choice are discussed later.

On the above basis, it has been possible to calculate rate constants for the reaction 3 for each of the carbonyls. These are given in Table 2 and fall in the range $11.5 < \log k < 12.3$. These values appear very reasonable in terms of the mass spectrometric time scale, in that, for a molecular ion to undergo a full sequence of CO eliminations in the ion source, the first of these reactions must have a high rate constant ($k > 10^{-9}$ s^{-1}) [6]. For reactions with such high rates an appreciable kinetic shift would be predicted, consistent with the observed "excess energy" values. The approximations used in deriving eqn. 1 mean that too much emphasis should not be placed on the numerical values of the rate constants, however, it is noteworthy that the carbonyls of nickel, iron and chromium show a trend [Fig. 1 (a)] consistent with the QET. That is, for molecules with values of ν and E_0 that are approximately constant, the kinetic shift

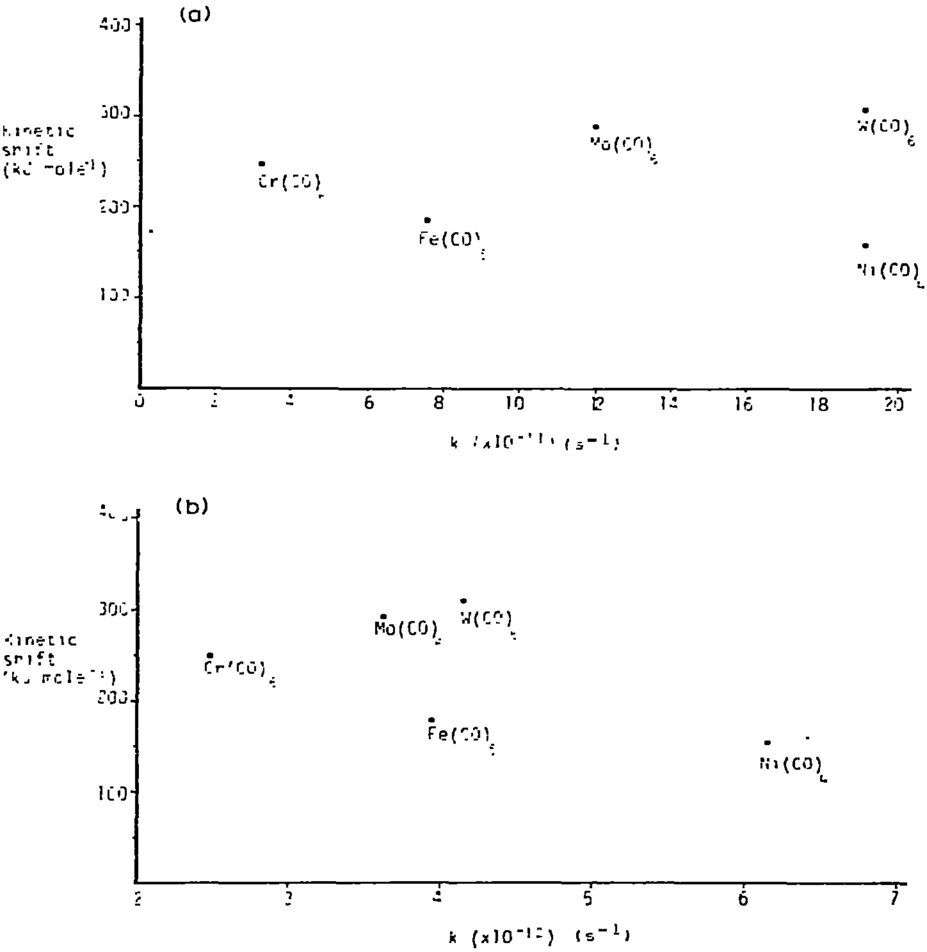

Fig. 1. Variation in rate constant with kinetic shift, (a) $s = 3n - 6$, (b) using the "sliding-scale" for $(s - 1) = (3n - 7)/x$.

increases with molecular size. Furthermore, there appears to be a definite trend in variation of rate constant with kinetic shift for the three Group VI metal carbonyls, suggesting that plots of rate constant versus internal energy, should have very similar shapes, as might be predicted for a series of closely related molecules undergoing identical fragmentation reactions. The shapes of log *k* vs. internal energy (*E*) curves for these three molecular ions are shown in Fig. 2. A comparison of the log *k* vs. *E* curves for molecular ions of nickel, iron and chromium carbonyls is given in Fig. 3. Again the results agree with experiment, in that, to achieve a given rate constant or narrow band of rate constants in order that the loss of the first molecule of CO may occur, the internal energy of the ions will increase in the order; $\mathrm{Ni(CO)_4}^{+} < \mathrm{Fe(CO)_5}^{+} < \mathrm{Cr(CO)_6}^{+}$ and a similar order of kinetic shifts would thus be predicted.

It must be pointed out that the initial portions of log *k* vs. *E* curves shown in Figs. 2 and 3 may not be entirely realistic as it may be more appropriate to take values of $s - 1$ equal to $(3n - 7)/x$, where x takes a value of five near the threshold and is unity at high internal energies. However, the form of each curve

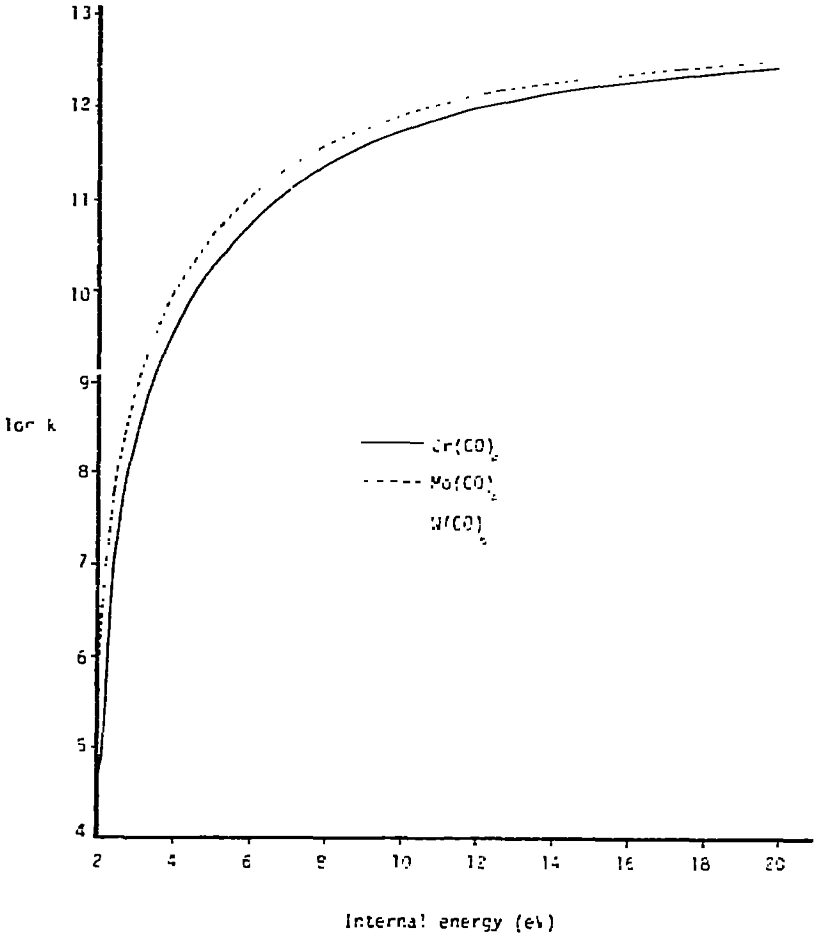

Fig. 2. Log *k* vs. internal energy (*E*) for $\mathrm{M(CO)_6}$ (M = Cr, Mo, W).

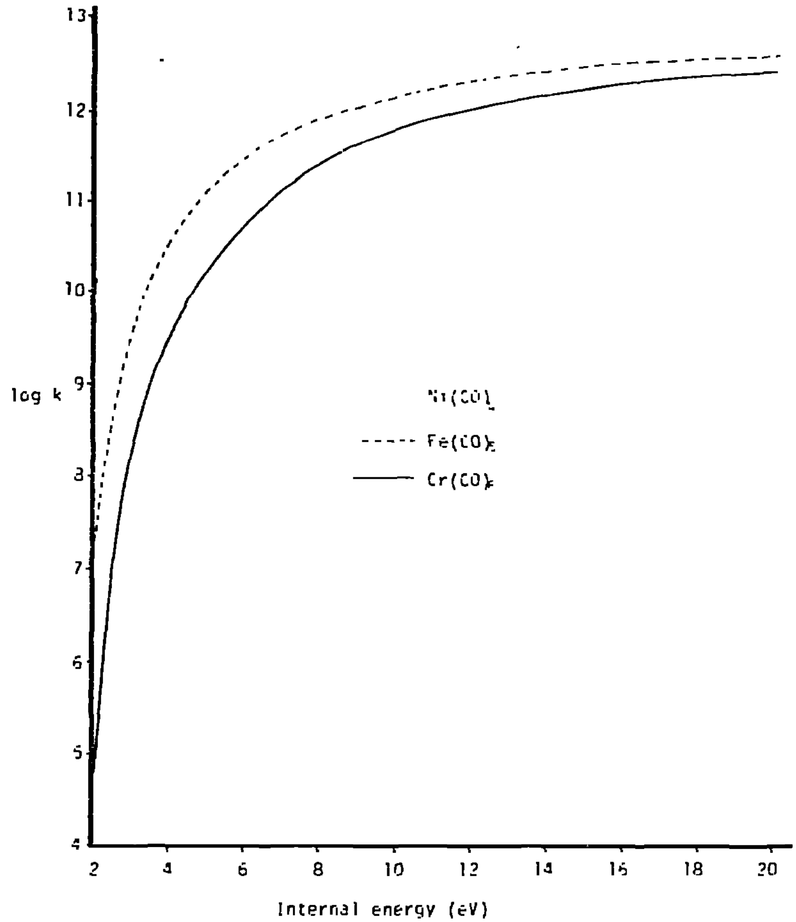

Fig. 3. Log *k* vs. internal energy (*E*) for Ni $(CO)_4$, $Fe(CO)_5$ and Cr $(CO)_6$.

remains essentially unaltered in region under discussion here and therefore the generalities discussed above are still valid. Previous studies [7] have taken $x = 5$ at the threshold and $x = 2$ at 10 eV in excess of the activation energy and have empirically allowed x to fall linearly with internal energy passing through these two points. Table 2 also shows results calculated by such an approach for each of the carbonyls. It is interesting to note that this leads to rate constants covering a much narrower range, however, the trends discussed above remain essentially unaltered [see, Fig. 1 (b)].

Thus, to summarise, the "excess energy" values found for heats of formation of metal atoms determined by mass spectrometry do not necessarily indicate that the metal ion is formed in excited state and, in fact such a postulate appears to be contrary to the QET. The above application of the QET to these systems is consistent with the "excess energies" being partitioned between the available oscillators in the respective molecular ions and further partitioned between ionic and neutral fragments upon successive decompositions. These excess energy values therefore represent the kinetic shifts on such measurements for mononuclear metal carbonyls.

Further work is in progress employing the more correct Rice—Ramsperger—Kassel—Marcus equation [5] in the calculation of kinetic shifts for molecules of this type.

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