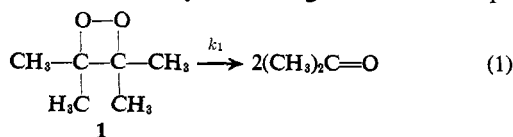


**Chemiluminescence of Tetramethyl-1,2-dioxetane. Measurement of Activation Parameters and Rates of Exceedingly Slow Reactions by a Simple and "Nondestructive" Method. Demonstration of Indistinguishable Activation Energies for Generation of Acetone Singlets and Triplets**

Sir:

Standard procedures for the measurement of rate constants and activation energies of unimolecular reactions<sup>1</sup> generally involve following the change of concentration of reactant or product with time. For example, the kinetics of thermal decomposition of tetramethyl-1,2-dioxetane (**1**) into two molecules of acetone (eq 1) has been studied by following both the disap-



pearance of **1** (nmr and uv analysis) and the appearance of acetone<sup>2</sup> (nmr analysis). Most standard methods<sup>3</sup> are relatively imprecise for small conversions (<1%) and are thereby severely limited in the region of temperature which can be employed for measuring the activation parameters. Thus, at 80°,  $t_{1/2}$  of reaction 1 is about  $7.8 \times 10^2$  sec, making the reaction rate inconveniently fast; at 40°  $t_{1/2}$  of reaction 1 is about  $1.4 \times 10^5$  sec, making the reaction rate inconveniently slow. We employ here a simple chemiluminescence method for determining reaction rates and activation parameters.<sup>4,5</sup> This method possesses the powerful advantage of being precise, amenable to use over a wide temperature range, and essentially "nondestructive" in the sense that during the time of analysis, the concentration of reactant does not change by an amount sufficient to be measured by most standard methods of analysis. Furthermore, we show that this technique can be applied to deduce information on the activation energy for generation of acetone singlets and triplets from **1**, and to set a lower limit to the enthalpy change of reaction 1.

(1) S. W. Benson, "The Foundation of Chemical Kinetics," McGraw-Hill, New York, N. Y., 1960.

(2) (a) N. J. Turro and P. Lechtken, *J. Amer. Chem. Soc.*, **95**, 264 (1973); H.-C. Steinmetzer, unpublished results. For other examples of measurements of dioxetane kinetics by nmr see (b) T. Wilson and A. P. Schaap, *J. Amer. Chem. Soc.*, **93**, 4126 (1971) and (c) W. H. Richardson, M. B. Yelvington, and H. E. O'Neil, *ibid.*, **94**, 1619 (1972). These studies span a temperature range of about 30°. For measurements employing infrared spectroscopy see (d) W. Adam and H.-C. Steinmetzer, *Angew. Chem., Int. Ed. Engl.*, **11**, 540 (1972).

(3) J. F. Bunnett in "Investigation of Rates and Mechanisms of Reactions," S. L. Fries, E. S. Lewis, and A. Weissberger, Ed., Interscience, New York, N. Y., 1961, p 177.

(4) For other examples of measuring kinetics of chemiluminescence methods, see (a) V. Y. Shyapintokh, O. N. Karpukhin, L. M. Postnikov, J. F. Tsipalov, A. A. Vichutinskii, and I. V. Zakharov, "Chemiluminescence Techniques in Chemical Reactions," Consultants Bureau, New York, N. Y., 1968; (b) R. F. Vasilev, *Russ. Chem. Rev.*, **39**, 529 (1970); (c) R. F. Vasilev, *Progr. React. Kinet.*, **4**, 305 (1967); (d) R. F. Vasilev, *Sov. Phys. Usp.*, **9**, 504 (1967); (e) I. Papisova, V. Y. Shyapintokh, and R. F. Vasilev, *Russ. Chem. Rev.*, **34**, 599 (1965).

(5) Activation energies from the effect of "quick temperature changes" have been employed to establish that no low activation energy path competes with the chemiexcitation state: (a) T. Wilson and A. P. Schaap, *J. Amer. Chem. Soc.*, **93**, 4126 (1971); (b) D. C.-S. Lee and T. Wilson, "Chemiluminescence and Bioluminescence," J. Lee, D. M. Hercules, and M. J. Cornier, Ed., Plenum Press, New York, N. Y., 1973; (c) T. Wilson, M. E. Landis, A. L. Baumstark, and P. D. Bartlett, *J. Amer. Chem. Soc.*, **95**, 4765 (1973). (d) The relationship of an apparent activation energy and the rate-determining step in a chemiluminescence sequence has been employed to obtain an apparent activation energy in bioluminescent systems: J. W. Hastings, Q. H. Gibson, and C. Greenwood, *Proc. Nat. Acad. Sci.*, **52**, 1529 (1964).

The kinetics of decomposition of **1** in the temperature range 40–70° can be measured in a conventional manner by monitoring the decrease of [**1**] by the change of chemiluminescence<sup>4,5</sup> intensity of either acetone fluorescence,  $I_F$  (eq 2), or phosphorescence,<sup>6</sup>  $I_P$  (eq 3).

$$I_F = k_1[\mathbf{1}]\phi_*^S\phi_F \quad (2)$$

$$I_P = k_1[\mathbf{1}]\phi_*^T\phi_P \quad (3)$$

The rate constant  $k_1$  refers to the total disappearance of a molecule of **1**,  $\phi_*^S$  (or  $\phi_*^T$ ) is the probability that a decomposed molecule of **1** will produce an excited singlet (or triplet) acetone, and  $\phi_F$  (or  $\phi_P$ ) is the probability that an excited singlet acetone will fluoresce (or that a triplet acetone will phosphoresce) under the reaction conditions. We can demonstrate the validity of eq 2 (or eq 3) by simply measuring  $I_F$  (or  $I_P$ ) as a function of [**1**].<sup>7</sup> Indeed, we found such plots of  $I_F$  or  $I_P$  vs. [**1**] were linear over the concentrations employed. Also, from eq 2 and 3 we note that under conditions such that [**1**] is constant (*i.e.*, its variation is smaller than the experimental error),<sup>8</sup>  $I_F$  and  $I_P$  are constant (within our experimental error) at a given temperature. In Figure 1 a typical "step function" of  $I_F$  or  $I_P$  is plotted at various temperatures.<sup>5</sup>

We see from eq 2 and 3 that variation in temperature may effect  $I_F$  or  $I_P$  by influencing (a) the value of  $k_1$ , (b) the excitation probability, or (c) the emission yield. However, we can measure the temperature coefficient (plot of a measured value vs.  $1/T$ ) of  $k_1$  by studying the effect of temperature on the rate of total disappearance of **1** by conventional techniques (nmr or uv analysis) and we can independently measure the temperature coefficient of  $\phi_F$  and  $\phi_P$  under our reaction conditions (by photoexcitation of acetone). Thus, by measuring the temperature coefficients of  $I_F$  and  $I_P$ , we can deduce (eq 2 and 3) the temperature coefficient of  $\phi_*^S$  and  $\phi_*^T$ . These ideas are summarized in Figure 2. The key notion in the analysis to follow is that three factors,  $k_1$ ,  $\phi_*^S$ , and  $\phi_F$  (or  $k_1$ ,  $\phi_*^T$ ,  $\phi_P$ ), determine the temperature dependence of  $I_F$  (or  $I_P$ ). The temperature dependences of  $k_1$  and  $\phi_F$  or  $\phi_P$  can be determined independently. In order to obtain the net apparent activation energy for chemiluminescence we can plot  $\ln I_F$  (or  $I_P$ ) vs.  $1/T$  in the usual manner.<sup>1</sup> In Figure 3 a plot of  $\log I_F$  or  $\log I_P$  vs.  $1/T$  is seen to be linear.

We now identify the measured temperature dependence of  $I_F$  or  $I_P$  with an apparent activation energy  $\Delta E(I_F)$  or  $\Delta E(I_P)$  and note that the latter quantities are equal to the sum of the apparent activation energies preceding the emission step, *i.e.*

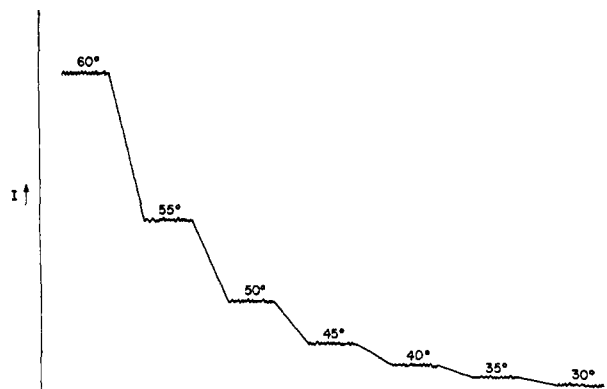
$$\Delta E(I_F) = \Delta E_1 + \Delta E_*^S + \Delta E_F \quad (4)$$

$$\Delta E(I_P) = \Delta E_1 + \Delta E_*^T + \Delta E_P \quad (5)$$

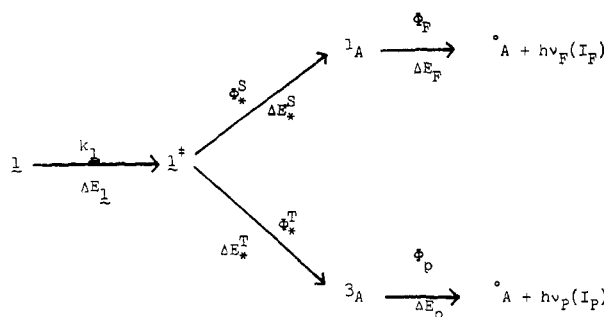
(6) The photoexcitation and chemiexcitation of acetone phosphorescence in acetonitrile solution are, contrary to expectations based on literature reported, quite easily observable: N. J. Turro, H.-C. Steinmetzer, and A. Yekta, *J. Amer. Chem. Soc.*, **95**, 6468 (1973).

(7) In eq 2,  $I_F$  is chemiluminescence from **1** due to essentially pure acetone fluorescence, achieved by either oxygenating an acetonitrile solution of **1** or adding a selective acetone triplet quencher (1,3-pentadiene or acrylonitrile).  $I_P$  is chemiluminescence from **1** due to essentially pure acetone phosphorescence and is achieved by simply purging acetonitrile solutions of **1** with nitrogen.<sup>6</sup>

(8) For example, we are able to make accurate measurements of  $I_P$  at 263°K. At this temperature we calculate  $k_1 = 10^{-9}$  sec<sup>-1</sup>, the half-time of reaction being approximately 100 years. Since we start with an approximately  $10^{-2}$  M solution of **1** during the time of analysis (~100 sec) we have decomposed about 10<sup>-5</sup>% of our sample!



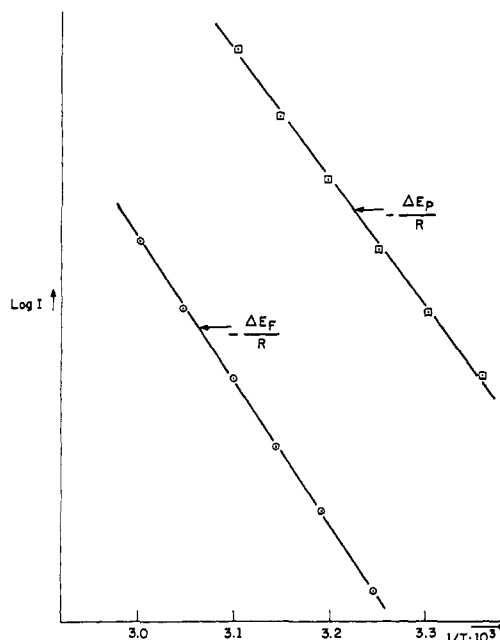
**Figure 1.** "Step function" analysis of the chemiexcited acetone fluorescence from oxygenated acetonitrile solutions of tetramethyl-1,2-dioxetane. The chemiluminescence intensity is in arbitrary units.



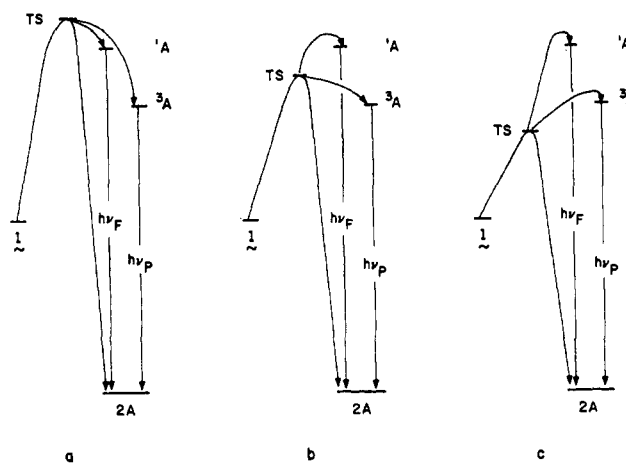
**Figure 2.** Model for the thermal decomposition of **1**.  $\Delta E_1$  is the temperature coefficient (activation energy) for disappearance of **1**,  $\Delta E_*^S$  ( $\Delta E_*^T$ ) and  $\Delta E_F$  ( $\Delta E_T$ ) are the temperature coefficients of excitation of singlet (triplet) acetone and of fluorescence (phosphorescence), respectively.

Experimentally, for the temperature range studied, it is found that the temperature coefficient for disappearance of **1** (the Arrhenius activation energy in this case) is 27.9 kcal/mol, that  $\phi_F$  has a negligible temperature coefficient ( $0.0 \pm 0.2$  kcal/mol), and that  $\phi_P$  has a *negative* temperature coefficient of  $-2.6$  kcal/mol. The temperature coefficients of  $I_F$  and  $I_P$  were found to be 27.7 and 25.2 kcal/mol, respectively (Figure 3). From the above data we see that the temperature coefficients of  $\phi_*^S$  and  $\phi_*^T$  must both be equal to zero, within our estimated experimental error of  $\pm 0.3$  kcal/mol, *i.e.*,  $\Delta E_*^S = (27.7 - 27.9) = -0.2$  kcal/mol and  $\Delta E_*^T = (27.7 - 25.2 - 2.6) = 0.1$  kcal/mol.

Now consider (Figure 4) our data in light of these models for the energetic positions for the transition states (TS) for irreversible disappearance of **1** relative to acetone (A), excited singlet acetone ( $^1A$ ), and triplet acetone ( $^3A$ ). Three choices exist: (a) TS is higher in energy than both  $^1A$  and  $^3A$ ; (b) TS is intermediate, being lower in energy than  $^1A$  and higher in energy than  $^3A$ ; (c) TS is lower in energy than both  $^1A$  and  $^3A$ . Choice three is ruled out on the basis of the very high (nearly quantitative) yield of  $^3A$  previously reported<sup>2</sup> and the identity of the activation energies from standard and chemiluminescence analyses. In other words, the major path for disappearance is on the pathway to  $^3A$  formation and therefore must possess a TS which is equal to or higher in energy than that of  $^3A$ . This expectation is fully consistent with our independent con-



**Figure 3.** Activation energies of chemiexcited acetone fluorescence ( $\odot$ ) and acetone phosphorescence ( $\square$ ) from step function analysis of chemiluminescence intensity.



**Figure 4.** Model a: position of TS is above  $^1A$  and  $^3A$ . Model (b): position of TS is between  $^1A$  and  $^3A$ . Model (c): position of TS is below  $^1A$  and  $^3A$ .

clusion that  $\Delta E_*^T$  is zero, and serves as further support for the validity of the methods reported here. Of the two remaining choices, our data support model a rather than model b, because  $\Delta E_*^S$  is also equal to zero, *i.e.*, there is no further activation in proceeding from TS to  $^1A$ . Since we must now conclude that *both*  $^1A$  and  $^3A$  are lower in energy than TS, we can place a lower limit on the  $\Delta H^0$  of reaction 1. The activation energy of **1** is  $\sim 27$  kcal/mol and the singlet energy of  $^1A$  is  $\sim 85$  kcal/mol. Since  $\Delta H_0 + \Delta H^\ddagger \geq 85$  kcal/mol, from our analysis  $\Delta H_0 \geq 58$  kcal/mol. Indeed, a recent direct measurement<sup>10</sup> of  $\Delta H_0$  was made and  $\Delta H_0$

(9) The values of enthalpy ( $\Delta H$ ) or energy ( $\Delta E$ ) are within 1–2 kcal/mol of each other in the temperature range we are considering.

(10) (a) P. Lechtken and G. Hohne, *Angew. Chem., Int. Ed. Engl.*, **12**, 772 (1973); (b) A. Schmidt, Columbia University, unpublished results; (c) the measured value of  $\sim 65$  kcal/mol is close to the calculated values of 69 kcal/mol: H. E. O'Neal and W. H. Richardson, *J. Amer. Chem. Soc.*, **92**, 6553 (1970); **93**, 1828 (1971).

was found to be  $\sim 65$  kcal/mol in complete consistency with our conclusions.

In summary, measurement of the direct chemiluminescence from reaction 1 as a function of temperature allows us to conclude that neither formation of  $^1A$  nor  $^3A$  is activated beyond the activation required to achieve the transition state for disappearance of **1**. This in turn implies that the latter TS possesses a higher energy content than  $^1A$  or  $^3A$  and that  $\phi_{*T}/\phi_{*S}$  is temperature independent.<sup>11</sup>

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(11) Although we have confidence in the reliability of the data reported here, we should point out that in certain solvents an apparently catalyzed, nonchemiluminescence pathway may dominate the decomposition of dioxetane. An experimental clue to the occurrence of this complication is the observance of very low activation energies ( $\Delta E < 20$  kcal/mol).<sup>6b,c</sup> We feel that the high activation energies, relative to previous reports and the demonstration of high yields of excited states, make the possibility of catalytic paths in our system very unlikely.

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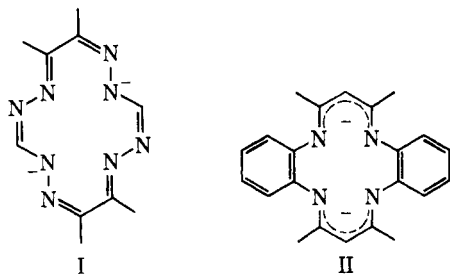
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### A New Route to the Formation of Organocobalt(III) and Organoiron(III) Complexes. Alkylation *via* Oxidative Deamination of Organic Hydrazines

Sir:

Considerable attention has been focused on the formation of cobalt(III)-carbon bonds during the past 10 years.<sup>1-5</sup> The routes to organocobalt(III) complexes are contained in a recent comprehensive review.<sup>6</sup> We report herein a new route to the formation of stable organometallic complexes from organic hydrazines and cobalt or iron complexes of quadridentate or macrocyclic ligands, two of which are shown below.<sup>7</sup>



(1) J. Halpern and J. P. Maher, *J. Amer. Chem. Soc.*, **87**, 5361 (1965); **86**, 2311 (1964).

(2) T. S. Roche and J. F. Endicott, *J. Amer. Chem. Soc.*, **94**, 8622 (1972).

(3) G. N. Schrauzer, *Accounts Chem. Res.*, **1**, 97 (1968).

(4) (a) D. Dolphin and A. W. Johnson, *Chem. Commun.*, 494 (1965);

(b) Schrauzer and J. Kohnle, *Chem. Ber.*, **97**, 3056 (1964).

(5) J. Kwiatek and J. Seyler, *J. Organometal. Chem.*, **3**, 421 (1965).

(6) D. Dodd and M. D. Johnson, *J. Organometal. Chem.*, **52**, 1 (1973).

(7) Bis(dimethylglyoximate), *N,N*-ethylenebissalicylideneiminato, and 6,7,13,14-tetramethyl-1,2,4,5,8,9,11,12-octaazacyclotetradeca-5,7,12,14-tetraene complexes of cobalt undergo similar reactions with some organic hydrazines.

Organic hydrazines are usually not considered to be alkylating agents. However, they are easily oxidized, going through diazene intermediates.<sup>8</sup> These diazenes can be oxidized further or they can decompose spontaneously to molecular nitrogen and organic radicals.<sup>9</sup> The oxidation of organic hydrazines is catalyzed by transition metals,<sup>10</sup> and the possibility of trapping the resulting organic fragments by suitable transition metal complexes, especially of cobalt, appeared highly likely.<sup>10a</sup>

The organocobalt(III) complexes are formed simply by the addition of the appropriate organic hydrazine to a solution of the cobalt(II) complex, followed by the addition of 1 atm of oxygen. During the ensuing exothermic reaction, molecular nitrogen is evolved and the organocobalt(III) complexes are formed. The reactions are normally carried out in acetonitrile and the complexes are precipitated by the addition of water. Yields are generally high and nearly quantitative with the cobalt(II) complex of **I**. Five-coordinate complexes of the type Co(I)R have been isolated using hydrazines where R =  $-\text{CH}_3$ ,  $-\text{CH}_2\text{CH}_3$ ,  $-\text{CH}_2\text{CH}_2\text{CH}_3$ ,  $-\text{CH}(\text{CH}_3)_2$ ,  $-\text{COCH}_3$ ,  $-\text{COOC}_2\text{H}_5$ ,  $-\text{C}_6\text{H}_5$ , and  $-\text{CH}_2\text{-C}_6\text{H}_5$  (Table I).<sup>11</sup> Although the greatest variety of

Table I. Some of the New Complexes and Their Nmr Spectra

Compound <sup>a</sup>	Nmr (in CDCl <sub>3</sub> ) <sup>b</sup>
[Co(I)CH <sub>3</sub> ]	7.96(s, 2); 2.69(s, 6); 2.42(s, 6); 0.04(s, 3)
[Co(I)C <sub>2</sub> H <sub>5</sub> ]	7.96(s, 2); 2.68(s, 6); 2.43(s, 6); 1.28(q, 2); -0.20(t, 3)
[Co(I)CH <sub>2</sub> C <sub>2</sub> H <sub>5</sub> ]	7.93(s, 2); 2.70(s, 6); 2.43(s, 6); 1.12 (t, 2); 0.8-1.8(m, 2); 0.55(t, 3)
[Co(I)CH(CH <sub>3</sub> ) <sub>2</sub> ]	7.97(s, 2); 2.69(s, 6); 2.43(s, 6); 1.6- 2.2(m, 1); -0.03(d, 6)
[Co(I)CH(CH <sub>3</sub> )(C <sub>6</sub> H <sub>5</sub> )]	7.97(s, 2); 2.68(s, 6); 2.43(s, 6); 1.0- 2.4(m, 3); 0.62(t, 3); -0.18(d, 3)
[Co(I)C <sub>6</sub> H <sub>5</sub> ]	8.25(s, 2); 2.82(s, 6); 2.52(s, 6); 5.6- 6.1, 6.5-6.9, 7.3-7.4 (m, 5)
[Co(I)CH <sub>2</sub> C <sub>6</sub> H <sub>5</sub> ]	8.05(s, 2); 2.55(s, 6); 2.30(s, 6); 1.8- 2.4(m, 2); 6.4-7.4 (m, 5)
[Co(I)COCH <sub>3</sub> ]	7.93(s, 2); 2.72(s, 6); 2.45(s, 6); 2.02 (s, 3)
[Co(I)CO <sub>2</sub> C <sub>2</sub> H <sub>5</sub> ]	8.17(s, 2); 2.83(s, 6); 2.52(s, 6); 3.18 (q, 2); 0.83(t, 3)

<sup>a</sup> (I) = C<sub>10</sub>H<sub>14</sub>N<sub>8</sub>. <sup>b</sup> Numbers in parentheses refer to the integrated intensity of the absorptions. The meaning of the symbols is as follows: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet.

organocobalt(III) complexes has been obtained with ligand **I**, we have been successful in obtaining at least methyl and ethyl derivatives with a variety of other ligands.<sup>7</sup> The new complexes of ligands **I** and **II** are five coordinate, whereas those of ref 7 are generally six coordinate and are identical in all respects with the

(8) E. M. Kosower, *Accounts Chem. Res.*, **4**, 193 (1971).

(9) M. N. Ackermann, M. R. Hallmark, S. K. Hammond, and A. N. Roe, *Inorg. Chem.*, **11**, 3076 (1970).

(10) H. Aebi, B. Dewald and H. Suter, *Helv. Chim. Acta*, **48**, 656 (1965).

(10a) NOTE ADDED IN PROOF. A reaction similar to that described here has recently been reported (P. Braunstein, *J. Chem. Soc., Chem. Commun.*, 851 (1973), in which aryl-gold(III) complexes are formed by the reaction of tetrachloro- or tetrabromoaurate(III) with phenylhydrazine hydrochloride.

(11) All compounds reported gave satisfactory elemental analyses and the parent peak for each was observed in high resolution mass spectrum.