

For a combinational quenching mechanism, the intensity SV equation is

$$K_{SV}^{app} = [(\phi_0/\phi)_{corr} - 1]/[Q] = (K_{SV} + \beta K_{eq}) + K_{SV}(\beta K_{eq})[Q] \quad (1)$$

where K_{SV}^{app} is the apparent intensity SV quenching constant and K_{SV} is the true SV quenching constant. β varies from 1.000 for measurements made under optically dilute conditions to $(\epsilon_{DQ}/\epsilon_D)$ for optically dense solutions. ϵ is the molar extinction coefficient, and the subscript DQ and D represent values for the association pair and donor, respectively, taken at the excitation wavelengths. Equation 1 holds if the donor concentration is much less than $[Q]$, which is satisfied in our experiments.

From the limiting value of K_{SV}^{app} at low concentrations of CuSO_4 in O_2 -saturated solutions, $K_{SV}^{\text{O}_2} + \beta K_{eq} \sim 325 \text{ M}^{-1}$. Since $K_{SV}^{\text{O}_2} = K_{SV}^{\text{N}_2}/6.15 = 55 \text{ M}^{-1}$, $\beta K_{eq} \sim 270 \text{ M}^{-1}$. Solid curve D is calculated from these two values and eq 1. Using βK_{eq} and $K_{SV}^{\text{N}_2}$, curve B is obtained. In both cases there is virtually perfect agreement between the N_2 and O_2 saturated results and the theoretical curves. It should be stressed that these two curves are computed only from $K_{SV}^{\text{N}_2}$, K_{SV}^{app} for O_2 saturated solutions at low concentrations of quencher and the O_2 dependence of τ . It thus seems probable that the combination of diffusional and static mechanisms is the only reasonable one which can successfully account for all data.

Since our solutions were optically dilute ($A \sim 0.02$), $\beta = 1$, and $K_{eq} \sim 270 \text{ M}^{-1}$. Thus, K_{eq} was obtained without recourse to any of the conventional techniques for measuring K_{eq} 's.

As an independent check of the existence of static quenching, we then monitored the absorption spectra of solutions containing both donor and CuSO_4 . The $\text{Ru}(\text{phen})_2(\text{CN})_2$ CT band moved $\sim 10 \text{ nm}$ to higher energy on addition of Cu^{2+} ($1.6\text{--}16 \times 10^{-3} \text{ M}$), which demonstrates association. No isosbestic points were observed, however, which suggests formation of both a 1:1 and 2:1 copper-ruthenium adduct.

The most reasonable mechanism of association is coordination of $\text{Ru}(\text{phen})_2(\text{CN})_2$ to the Cu^{2+} through the free end of the CN. Several lines of evidence support this. Only substitutionally labile species (Cu^{2+} , Ni^{2+} , and Co^{2+}) statically quench $\text{Ru}(\text{phen})_2(\text{CN})_2$.⁸ Also other neutral ruthenium(II) complexes without coordinated CN only quench dynamically.⁹ Finally, CN's can form bridging ligands between metal ions in solution and the solid state.¹⁰ Since luminescence is certainly terminated by the presence of one bonded Cu^{2+} , our measured K_{eq} represents the first association constant. Our absorption data do not permit us to evaluate the second but suggest its value is not greatly different from that of the first.

The static quenching could be by nearest neighbors rather than by chemical association. The low concentration of quencher, however, makes this at most a minor pathway.¹¹

(8) J. N. Demas, J. W. Addington, D. Diemente, and E. Harris, manuscript in preparation.

(9) J. N. Demas, D. Diemente, and J. Bowman, manuscript in preparation.

(10) D. F. Shriver, *Struct. Bonding (Berlin)*, 1, 32 (1966).

(11) P. J. Wagner and I. Kochevar, *J. Amer. Chem. Soc.*, 90, 2232 (1968).

It should be noted that an expression functionally identical with eq 1 results when quenching occurs from both the emitting state and an upper state which is precursor to the emitting one. We rule this possibility out, since decay time measurements show that any upper state must have a decay at least 10^2 times faster than the emitting level. Thus, quenching of the upper level could not be significant under our conditions.

Schilt demonstrated the protonation of $\text{Fe}(\text{bipy})_2(\text{CN})_2$ and $\text{Fe}(\text{phen})_2(\text{CN})_2$ in solution.¹² Based on the blue shift of the absorption spectrum on protonation, he argued that H^+ directly attacks the Fe^{2+} rather than the CN. The very similar spectral changes in the $\text{Ru}(\text{phen})_2(\text{CN})_2\text{--Cu}^{2+}$ system suggest that this argument is incorrect, since the bulky Cu^{2+} cannot attach itself to the Ru^{2+} directly.

Our results clearly stress the importance of combining both τ and ϕ quenching data to obtain a full understanding of the photo and chemical processes in systems involving luminescent metal complexes. Also, these results demonstrate an unusual technique for studying equilibria involving transition metal complexes. We are currently constructing a nanosecond decay time apparatus to determine ion-pairing constants between metal complexes by these methods.

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(12) A. A. Schilt, *J. Amer. Chem. Soc.*, 82, 3000 (1960).

J. N. Demas,* J. W. Addington
Chemistry Department, University of Virginia
Charlottesville, Virginia 22901
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Organic Reactions at High Pressure. Cycloadditions of Enamines and Dienamines¹

Sir:

The use of very high pressures for preparative organic chemistry has been relatively little explored.² The pressure dependence of the rate constant of the reaction is $\delta \ln k/\delta p = -\Delta V^\ddagger/RT$. If ΔV^\ddagger , the activation volume, is negative, *i.e.*, if the formation of the activated complex from the reactants results in overall contraction, the rate k will increase with increasing pressure.² The effect of pressure on the rate of several Diels-Alder reactions has been determined and found to provide a large acceleration, the ΔV^\ddagger being between -25 and $-38 \text{ cm}^3/\text{mol}$.³

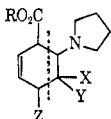
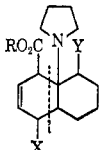
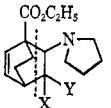
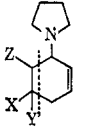
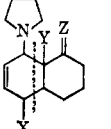
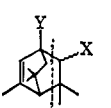
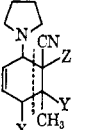
We would like to report our results which show that high pressure (8–20 kbars, 7895–19,738 atm) is a valu-

(1) This research was supported by National Science Foundation Grant No. GP-8700.

(2) (a) For some reviews of the physics and chemistry of high pressure, see P. W. Bridgman, "Physics of High Pressure," G. Bell and Sons, London, 1952; (b) W. J. le Noble, *J. Chem. Educ.*, 44, 729 (1967); (c) K. B. Weale, "Chemical Reactions at High Pressures," E. & F. N. Spon, London, 1967; (d) W. J. le Noble, *Progr. Phys. Org. Chem.*, 5, 207 (1967).

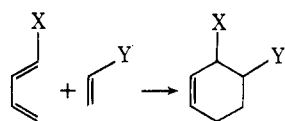
(3) For a general review, see V. D. Brück, R. Bühler, C. C. Henck, H. Plieninger, K. E. Weale, J. Westphal, and B. Wild, *Chem.-Zt.*, 94, 183 (1970).

Table I. Product Types Obtained from High Pressure Cycloaddition

	Product ^a	% yield ^b	Pressure (kbar) ^c	(Time)
	1, R = CH ₃ ; X = H; Y = CH ₃ ; Z = H	88 ^{d,e}	10	(18 hr)
	2, R = CH ₃ ; X = Y = CH ₃ ; Z = H	63 ^{d,f}	8.8	(15 hr)
	3, R = CH ₃ ; X, Y = -(CH ₂) ₅ -; Z = H	84 ^{g,h}	15	(22 hr)
	4, R = C ₂ H ₅ ; X = Y = CH ₃ ; Z = CH ₃	No reaction	12	(28 hr)
	5, R = CH ₃ ; X = H; Y = CH ₃	90	15.2	(22 hr)
	6, R = C ₂ H ₅ ; X = CH ₃ ; Y = H	90 ⁱ	15	(24 hr)
	7, X = H; Y = CH ₃	No reaction	14	(24 hr)
	8, X = Y = CH ₃	No reaction	14	(24 hr)
	9, X = Y = H; Z = CO ₂ C ₂ H ₅ ; diethylaminodienamine	95 ^j	13.6	(30 min)
	10, X = H; Y = CH ₃ ; Z = CO ₂ CH ₃	85	11.3	(20 hr)
	11, X = H; Y = -CH ₂ CH(CH ₃)(CH ₂) ₂ CH=C(CH ₃) ₂ ; Z = CO ₂ C ₂ H ₅	70	14	(26 hr)
	12, X = H; Y = CH ₃ ; Z = COCH ₃	81	9.6	(8 hr)
	13, X = Y = CH ₃ ; Z = COCH ₃	No reaction	9.6	(25 hr)
	14, X = Y = CH ₃ ; Z = CN	No reaction	13.2	(26 hr)
	15, X = H; Y = CHO; Z = H,H	71	9.4	(24 hr)
	16, X = CH ₃ ; Y = CHO; Z = H,H	18	14.5	(24 hr)
	17, X = H; Y = COCH ₃ ; Z = H,H	80	13.0	(11 hr)
	18, X = Y = H; Z = O	47 ^{g,k}	8.4	(18 hr)
	19, X = CO ₂ CH ₃ ; Y = morpholino	53 ^l	15.8	(7.5 hr)
	20, X = CN; Y = piperidino	90 ^l	8.4	(13 hr)
	21, X = H; Y = (CH ₂) ₄ CH ₃ ; Z = CO ₂ C ₂ H ₅	90 ^m	10	(1 hr)
	22, X = CH ₃ ; Y = (CH ₂) ₄ CH ₃ ; Z = CO ₂ C ₂ H ₅	90 ⁿ	13	(35 min)
	23, X = CH ₃ ; Y = (CH ₂) ₂ CH(CH ₃)CH=CH ₂ ; Z = CO ₂ C ₂ H ₅	100 ⁿ	20	(10 min)
	24, X = CH ₃ ; Y = (CH ₂) ₂ CH(CH ₃)CH=CH ₂ ; Z = CN	90 ⁿ	13	(3.5 hr)

^a Dashed line denotes position of reaction. Satisfactory spectral data and elemental analyses were obtained. ^b Yields are isolated yields unless indicated otherwise. No attempt was made to optimize conditions. ^c The pressure was measured by a Heise gauge and is the applied pressure. ^d Isolated and analyzed as diene. ^e Yield of 80% at atmospheric pressure, 80°, 12 hr. ^f Yield of 26% at atmospheric pressure, 90°, 36 hr. ^g This compound readily lost pyrrolidine on distillation and was analyzed as a corresponding diene. ^h Yield of 53% for related 5,4-spiro analog, atmospheric pressure, 80°, 20 hr. ⁱ Yield of 14% at atmospheric pressure, 80°, 24 hr. ^j Yield of 94% at atmospheric pressure, 20°, 144 hr. ^k Yield of 16% atmospheric pressure, 20°, 72 hr. ^l Mixture of endo and exo exomers. ^m Yield of 90% at atmospheric pressure, 20°, 24 hr. ⁿ Yields determined by nmr.

able tool to aid the reaction of enamines and dienamines with activated dienes and olefins, respectively.⁴ Although it has not been clearly established whether these



- a, X = CHO, COCH₃, CO₂R; Y = NR₂
 b, X = NR₂; Y = CHO, COCH₃, CO₂R

cycloadditions follow a concerted route or a stepwise ionic process,⁵ a net volume contraction is expected for

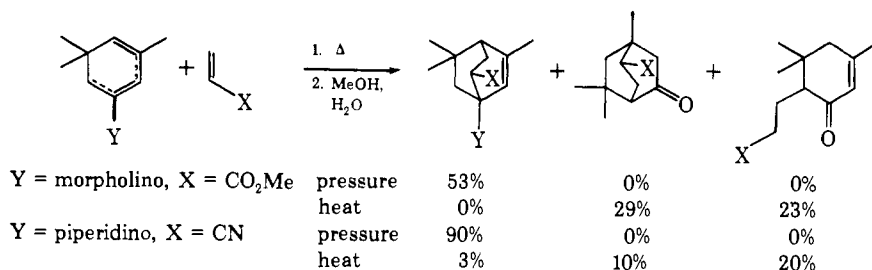
(4) For related reactions at atmospheric pressure, see (a) S. Danishefsky and R. Cunningham, *J. Org. Chem.*, **30**, 3676 (1965); (b) G. A. Berchtold, J. Ciabattini, and A. A. Tunick, *ibid.*, **30**, 3679 (1965); (c) S. Hunig and H. Kahanek, *Chem. Ber.*, **90**, 238 (1957).

(5) A. G. Cook, "Enamines," Marcel Dekker, New York, N. Y., 1969.

the conversion of double bonds to single bonds as the reactants approach the transition state.^{2d}

The reactions were conducted in a single stage piston-cylinder apparatus with "O"-ring and delta-ring seal using kerosene as the pressure transmitter. An ethereal solution of equimolar quantities of the reactants was placed in a compressible copper-beryllium bellowed tube and kept under hydrostatic pressure (8–20 kbars) at room temperature for the times indicated. The ether was rotary evaporated and the residue was distilled in a Kugelrohr apparatus. In most cases, analytically pure samples were obtained by this simple operation. The results of this study are summarized in Table I.

For the reaction of enamines with dienamic esters, the use of high pressure in contrast to normal thermal conditions generally permits the reaction to proceed in higher yield and in a shorter reaction time. These reactions are as simple to run under pressure as in standard glass-



ware equipment and can be performed on a 10–20-g scale. The effect of increased substitution to inhibit the cycloaddition reaction became apparent in the attempted reaction of ethyl sorbate with the pyrrolidine enamine of isobutyraldehyde (entry 4). The failure of ethyl cyclohexadienecarboxylate to react with the pyrrolidine enamine of propionaldehyde and isobutyraldehyde (entry 7 and 8) also might reflect the unfavorable electronic effect of an α -substituent.

For the reaction of dienamines with enoic esters, ene nitriles, and enones (*i.e.*, conjugated acceptors) again it was found that the cycloaddition proceeded well at room temperature and generally in higher yield and shorter reaction time than the thermally induced process. In the pressure range studied, similar steric and/or electronic effects of the added β -substituent in the conjugate acceptor were found; *i.e.*, in going from pent-3-en-2-one (entry 12) to mesityl oxide (entry 13) the reaction was inhibited. Of particular interest was the finding that under pressure the reaction of isophorone dienamine with methyl acrylate (entry 19) and with acrylonitrile (entry 20) yielded only the Diels–Alder type adduct. These same reactions have been studied thermally and found to give different product distributions.⁶ Thus, the use of high pressure can effect a change in the course of a reaction as well as provide product specificity.

A sensitivity of the cycloaddition to pressure was found for entry 11; at 9.8 kbar pressure none of the desired product was obtained but at 13.9 kbar pressure the product was obtained in 70% yield. This pressure dependency warrants further study, especially in those cases where no product was obtained.

The last four examples (entries 21–24) involve the preparation of hindered systems. It was found that by double activation of the conjugate acceptor it was possible to overcome the deleterious effect of two β -substituents. The reaction of 1-pyrrolidino-1,3-butadiene with ethyl 2-cyano-3-methyl-2-octenoate can, in fact, be done at atmospheric pressure and room temperature. However, this cyano ester failed to react with 1-pyrrolidino-1,3-pentadiene even at 80° for a prolonged period. This latter reaction was effected in quantitative yield at 20 kbar pressure in 10 min. Attempts to purify the products of the last four reactions by preparative vpc or Kugelrohr distillation at reduced pressure resulted in retrocycloaddition.

The use of high pressure is extremely valuable in those cases where steric hindrance to reaction or thermal instability of a reactant precludes the use of conventional means to accelerate sluggish reactions. Furthermore, in the pressure reaction the amino compound

(6) H. Nozaki, T. Yamaguti, S. Veda, and K. Kondo, *Tetrahedron*, **24**, 1445 (1968).

can be isolated if so desired; this is not possible for most thermal reactions.⁷

(7) The authors are greatly indebted to Mr. Duane Newhart for his assistance in the fabrication and maintenance of the pressure equipment and to Professor G. Jura for the hydraulic press equipment.

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William G. Dauben,* Alan P. Kozikowski[†]

Department of Chemistry, University of California
Berkeley, California 94720

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A Photoelectron Spectroscopic Study of Polyphosphines. The Question of $p\pi:d\pi$ Bonding

Sir:

Polyphosphines have been the subject of much recent attention.¹ Such compounds, unlike their monophosphine analogs, show intense uv absorption, and it has been generally believed^{2,3} that this is due to the delocalization of phosphorus lone pair electrons into higher orbitals of appropriate symmetry of juxtaposed phosphorus atoms. This model has, however, been questioned both on structural grounds⁴ and from consideration of electronegativity.⁵ Here we wish to report some preliminary results of a study of polyphosphines by photoelectron spectroscopy (pes) which have a bearing on this problem.

The observation of more than one peak in the phosphorus lone pair region for a cyclopolyphosphine can be attributed to interactions between the phosphorus lone pairs. In the case of (CF₃P)₄ (1) the molecular symmetry is known⁶ to be D_{2d} . Hence the MO's derived from the lone pairs are of symmetry B_2 , E, and A_1 , having the forms indicated in Figure 1. In A_1 , all four nearest neighbor interactions are antibonding, in B_2 all are bonding, while in E all such interactions are non-bonding. The order of increasing orbital energy, and so of decreasing ionization potential, should therefore be $B_2 < E < A_1$. Furthermore, the transannular interactions in A_1 and B_2 are bonding but in E antibonding; the A_1 –E separation should therefore be less than the E– B_2 one. The first three ionization potentials (I_1 , I_2 , I_3) follow this pattern and can be assigned respec-

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(2) W. Mahler and A. B. Burg, *J. Amer. Chem. Soc.*, **80**, 6161 (1958).

(3) L. R. Grant and A. B. Burg, *J. Amer. Chem. Soc.*, **84**, 1835 (1962).

(4) R. L. Kuczkowski, H. W. Schiller, and R. W. Rudolph, *Inorg. Chem.*, **10**, 2505 (1971).

(5) H. W. Schiller and R. W. Rudolph, *Inorg. Chem.*, **10**, 2500 (1971).

(6) G. J. Palenik and J. Donohue, *Acta Crystallogr.*, **15**, 564 (1962)