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B, Comparison of Corrins of Cobyric and Monocarboxylic Acid; Figures C–I, Results of Partitioned Matrix Analysis; Figures J–L, Results of Factor Analysis; Figure M, "Gate Post" atoms; Figure N, Movement of "Gate Post" atoms Unfolding; Figure O, Short H···H and H···O Distances; Figure P, Steric Factors Affecting Methyl Groups in Methylcobalamin; Figure Q, Co(III) and Co(II) Corrins; Figure R, Orientations of Upper Ligands in Some B_{12} Derivatives; Figures S and T, Rotation about the Glycosidic Bond (37 pages). Ordering information is given on any current masthead page.

Collisional Relaxation of Photoexcited Bromobenzene Ions by Various Neutral Partners

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Abstract: With use of the technique of competitive collisional quenching of two-photon dissociation, the collisional quenching of photoexcited bromobenzene ions was measured for 35 neutral partners. The number of collisions required for quenching ranged from 3.5 to 180, generally increasing with molecular complexity. For quench gases not containing unsaturation or heavy atoms (except H_2O), the quenching efficiency gives an excellent plot against $NM_r^{0.5}$, where N is the number of atoms in the neutral, and M_r is the reduced mass. Neutrals containing double or triple bonds, or heavier-than-third-row atoms, show markedly enhanced quenching efficiency. The results are compared with other quenching efficiency studies of polyatomic ions and neutrals and show similarities to several other studies which have been interpreted in terms of a collision-duration or energy-flow limitation on the rate of energy removal. The present results are not in accord with models assuming energy equilibration in the collision complex on each collision.

Intermolecular energy transfer in collisions, a common activation and deactivation process of excited molecules, plays an important role in many gas-phase reactions. The thermalization of vibrationally excited molecules is of particular interest in many aspects of gas-phase chemistry.

Study of the collisional quenching of vibrationally excited neutral molecules has a long history, but only more recently have techniques and interest developed in studying gas-phase ions. Because of the longer range and greater strength of ion–neutral interactions, compared with neutral–neutral interactions, one might expect that energy transfer in the ion case might tend to be more efficient, but not enough is known to give a general conclusion on this fundamental question. Several studies have looked at quenching of small ions, yielding absolute efficiencies[1-3]. Among polyatomic ions, the relative-efficiency study of Miasek and Harrison[4] and some dimer–ion stabilization studies in Bowers' laboratory[5,6] have looked at a variety of quenching neutrals, while several other studies using one or a few quench gases have been reported.[7-9]

We have reported some results[10-12] using the technique of competitive collisional quenching of two-photon photodissociation as a method having the capability of measuring the absolute quenching efficiency for some polyatomic ions. We describe here the results of a more extensive study with bromobenzene ion using enough different neutrals to make various trends clear. The vibrationally excited bromobenzene ions are created by 514.5-nm photon absorption, with the collisional quenching experiment giving the number of collisions required to reduce the ions from 20000 to 2850 cm^{-1} of internal energy.

Experimental Section

Instrumentation and experimental techniques for the determination of the two-photon pressure dependence in bromobenzene ion with ICR mass spectrometry have been previously described in detail.[11] Bromobenzene ions were formed by a 200-ms pulse of a nominally 11 eV electron beam. After irradiation by the Coherent Radiation I-12 argon ion laser at 514.5 nm for 1 s, the ions were sampled during a detect pulse of 4-ms duration. The pressure of bromobenzene was maintained at 2 × 10^{-8} Torr (ion gauge reading), while the pressure of the quench gas varied up to about 10^{-5} Torr (corrected). The ionization gauge pressure readings were converted into absolute pressure with use of published

Table I. Quenching Efficiencies

neutrals	ORC[a]	*Z*	neutrals	ORC[a]	*Z*
		Simple Molecules			
1. ^3He	6.1	181	10. CH_3Cl	13.8	27
2. ^4He	5.3	150	11. C_2H_6	9.83	24
3. Ne	3.5	100	12. C_2H_5F	13.9	19
4. Ar	5.34	77	13. C_2H_5Cl	13.2	19
5. H_2	14.75	160	14. c-C_3H_6	9.1	17
6. D_2	10.5	93	15. c-C_2H_4O	14.7	21
7. H_2O	6.86	8	16. *n*-C_3H_8	10.03	18
8. CH_4	9.91	40	17. *n*-C_4H_{10}	10.27	13
9. CH_3F	18.5	29	18. c-C_6H_{12}	8.05	8
		Unsaturated Molecules			
19. O_2	5.75	30	25. C_2H_2	9.05	12
20. N_2	6.69	70	26. C_2H_4	9.91	12.5
21. NO	6.08	28	27. C_3H_6	9.98	7
22. CO	6.36	40	28. *i*-C_4H_8	10.2	10
23. CO_2	6.5	18	29. c-C_6H_{10}	8.29	5.5
24. COS	9.8	8			
		Heavy-Atom Molecules			
30. Kr	5.05	30	32. CH_3Br	11.5	19
31. Xe	5.64	24	33. C_6F_5I	11.5	3.5

[a] ORC = orbiting rate constant (10^{-10} cm^3 molecule^{-1} s^{-1}).

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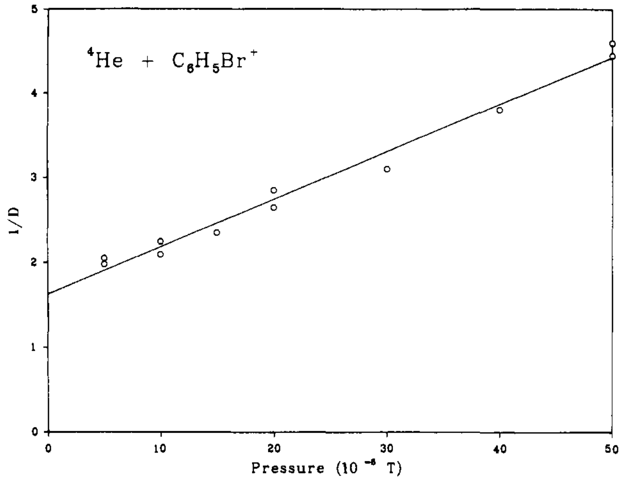

Figure 1. Stern–Volmer-type plot of inverse dissociation vs. quench-gas pressure for ^{4}He quench gas. The pressure scale is ion gauge pressure corrected as described in the text for ion gauge sensitivity.

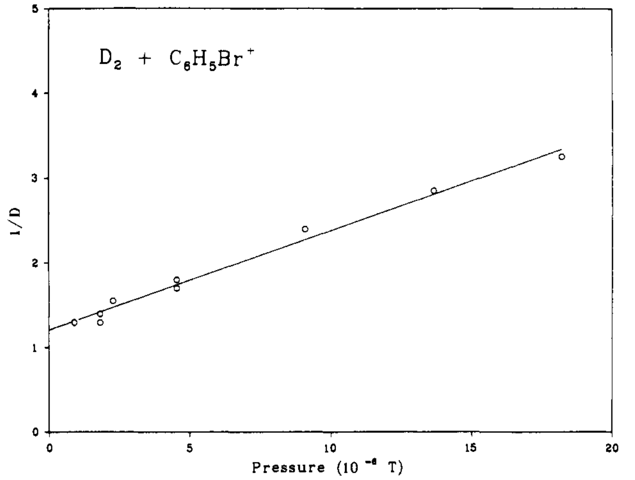

Figure 2. Plot as in Figure 1 for D_2 quench gas.

sensitivity factors.[13,14] Those polarizabilities not available in ref 13 and 14 were calculated theoretically following Miller and Savchik.[15] All chemicals were obtained from commercial sources and used without further purification except for the removal of noncondensable gases by several freeze–pump–thaw cycles.

Results

Determination of the quenching rate depends on observing the decrease in two-photon photodissociation as pressure increases and is based on the well-established kinetic analysis of bromobenzene ion two-photon dissociation.[11,16-18] The photodissociation kinetics can be described by

$$C_6H_5Br^{\bullet+} \underset{k_q[M]+k_0[C_6H_5Br]}{\overset{I\sigma_1}{\rightleftarrows}} C_6H_5Br^{\bullet+*} \xrightarrow{I\sigma_2} C_6H_5^+ + Br$$

$$1/D = \frac{I\sigma_1 + I\sigma_2 + k_q[M] + k_0[C_6H_5Br]}{I^2\sigma_1\sigma_2}$$

Here D is the dissociation, $D = -\ln$ [(light-on signal)/light-off signal)]. I is the light intensity, σ_1 and σ_2 are the cross sections

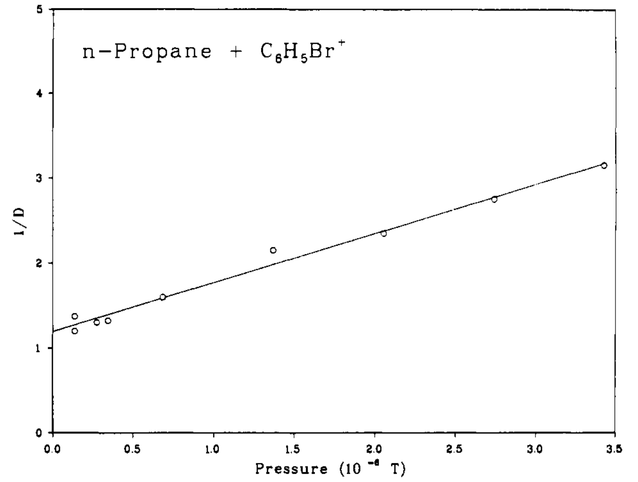

Figure 3. Plot as in Figure 1 for C_3H_8 quench gas.

for first and second photon absorption, k_q and k_0 are the rate constants for quenching by quench gas and by parent neutral, respectively, [M] is the concentration of quench gas, and [C_6H_5Br] is the parent neutral concentration.

Representative Stern–Volmer-type plots of $1/D$ vs. quench-gas pressure are shown in Figures 1–3. The curves are reasonably good straight lines whose slopes give the relative quenching rates. The data set was assembled by comparing pairs of quench gases under identical conditions on the same day, and the results of Table I for the quenching rate relative to methane were constructed from the series of direct comparisons.

The absolute quenching rate is available[11,17,18] from analysis of the slope and intercept of the Stern–Volmer line, and it was evaluated for some quench gases as a check on the relative results, and to fix the reference value for methane. However, since the absolute quenching-rate expression contains the square of the intercept, and the intercept itself is rather uncertain, the relative values obtained from the slope comparisons are considered more precise than the absolute values. The accuracy of the values relative to methane is probably limited by the accuracy of pressure determination and should be better than ±10%. (However, some quench gases, including H_2O, CO_2, and some alkyl halides, gave less reproducible results and are perhaps uncertain to 20%.)

The kinetic analysis leading to eq 1 is based on the quenching kinetics being a first-order kinetic process, which would be appropriate if a single collision were required for quenching. However, in fact a cascade of many collisions is required for quenching of the photoexcited ion below the one-photon threshold, and the rate-process kinetic analysis is not clearly appropriate. Extensive computer modeling of the relaxation in two-photon dissociation kinetics has been done by using a master-equation approach, and it has been shown that even if cascade kinetics are actually obeyed, the data may be analyzed with little error by the rate-process equations, and the inverse of the quenching rate constant derived from the analysis will be very close to the actual cascade quenching time.[19,20] This question will affect the absolute quenching-rate values, but it will have little influence on the relative rates for different quenchers.

A collision number Z was calculated by dividing the collision rate by the quenching rate. (Z, roughly speaking the number of collisions required to quench the excited ion, is the inverse of the frequently reported collision efficiency.) For nonpolar quench gases, the orbiting collision rate constants were calculated with the Langevin equation;[21] for polar quench gases ADO theory[22] was used, following the extrapolation method of Barker and Ridge.[23] The results are displayed in Table I.

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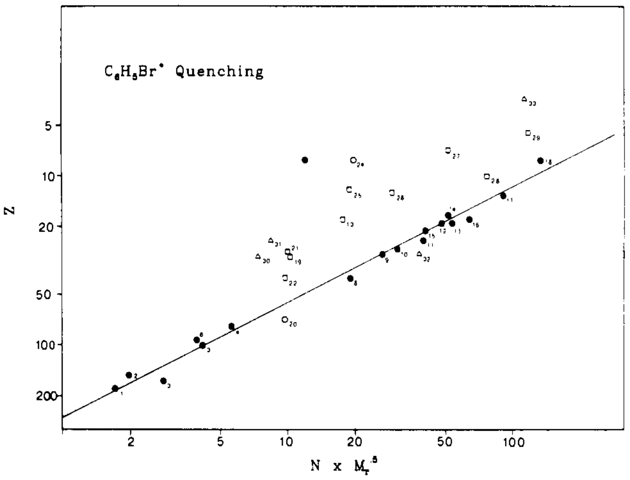

Figure 4. Plot of collision number Z vs. the parameter $n(m_r)^{1/2}$. The quench gases are keyed to Table I. Filled circles are saturated quench gases from the first group in Table I; squares are the unsaturated gases from the second group; and triangles are heavy-atom gases from the third group.

Table II. Isotope Effects

quench gas	ion	k_q[a]	Z	k_{orb}[a]
^3He	$C_6H_5Br^+$	0.034	181	6.1
^4He	$C_6H_5Br^+$	0.035	150	5.3
H_2	$C_6H_5Br^+$	0.093	160	14.8
D_2	$C_6H_5Br^+$	0.11	93	10.5
H_2	$C_6H_5I^{+}$[b]	0.07	210	14.8
D_2	$C_6H_5I^{+}$[b]	0.07	150	10.5

[a] 10^{-10} cm^3 molecule^{-1} s^{-1}. [b] Reference 12.

Discussion

A. Characteristics of Bromobenzene Ion Quenching. Overall, quenching efficiency increases with size and complexity of the quenching neutral, spanning a range of almost two orders of magnitude in Z values. It is clear that translational, rotational, and vibrational degrees of freedom of the neutral all can carry off energy. There is a reasonable correlation between the size of the quenching neutral and the quenching efficiency, as shown in Figure 4. Since the strength of the ion–neutral interaction, the heat capacity of the neutral, and the reduced mass (and thus the collision duration) all tend to increase with increasing neutral size, it is entirely natural that quenching efficiency increases with neutral size, without much regard to the mechanism of energy transfer.

Two principal factors may govern the quenching efficiency: the strength of the ion–neutral collision; and the heat capacity of the quenching neutral. These may in turn depend on a number of factors, including the collision duration and intimacy (which depend on the strength of the ion–neutral interaction and on the neutral mass), the number of energy accepting degrees of freedom of the neutral, the characteristics of these degrees of freedom, the possibility of close coupling through chemical interaction, and so forth. Separating these various factors is difficult, but a few observations can be made about their influence.

Mass Dependence. There are two comparisons in the data between quenching gases differing substantially in mass but similar in other properties: the H_2/D_2 comparison and the $^3He/^4He$ comparison. Table II summarizes these data. It is notable that in both cases the quenching rate constant is similar for the two isotopic species (although the slightly higher value for D_2 vs. H_2 is probably experimentally significant). This was also found to be the case[12] in comparing the quenching of iodobenzene ion with H_2 and D_2. Apparently the greater collision rate of the lighter isotope is offset by its lower energy transfer per collision, in all three cases.

This lends further support to the picture advanced previously in the iodobenzene case:[12] The lighter isotope collides with the ion more often than the heavier in the ratio $(M_h/M_l)^{0.5}$, but its velocity during the collision is greater by the same factor, so that (assuming similar collision path shapes) the overall fraction of the time the neutral spends in contact with the ion is the same for both isotopes.[24] This picture postulates that, in the case of the very inefficient quenchers H_2 and He, the transfer rate is governed by a rate-limiting slow transfer of energy from ion vibrational excitation to neutral translation (and rotation). That this process is slow and rate limiting is supported by the fact that, as shown below, less energy is transferred during each collision than if translation (and rotation) came to equilibrium with the ion internal temperature.

The neutral mass dependence observed for quenching of these large aromatic ions is in some contrast to that reported by Ferguson et al.[1] for quenching of O_2^+ by H_2 and D_2. They report substantially lower k_q and higher Z values for D_2 than for H_2. No good explanation of this large isotope effect has yet been advanced. They discuss their results in terms of formation of a complex between ion and neutral, but in the case of hydrogen quenching, the lifetime k^{-1} calculated from their data for the complex is less than 10^{-12} s. When the time of contact is so short, it seems more reasonable to speak in terms of a simple orbiting collision rather than formation and breakup of a complex, which leads to the line of argument presented above to rationalize our results; neither picture gives an obvious rationalization for the results on O_2^+.

Chemical Interactions. It is in general hard to isolate the effect of specifically chemical interactions from the more general effects of changing shape, polarizability, mass, moment of inertia, and vibrational frequencies of the different neutrals, but the data set offers several comparisons for which changes in all these factors are small and the effect of specific interactions is clear. These cases are the alkane/alkene pairs, specifically C_2H_6/C_2H_4, C_3H_8/C_3H_6, c-C_3H_6/C_3H_6, C_4H_{10}/C_4H_8, and c-C_6H_{12}/c-C_6H_{10}. In all cases the alkene is the more efficient quencher, and the effect is large. We attribute this to chemical interaction between the alkene π system and the π electrons and/or the halogen n electrons in the aromatic ion. An attractive, bonding interaction will deepen the ion–neutral potential well, lengthen the complex lifetime, and increase the extent of energy flow during the collision. These observations suggest that third-body stabilization of a bromobenzene ion/alkene complex might be easy. Acetylene is about equal in efficiency to ethylene, suggesting a similar degree of chemical interaction with double and triple bonds.

The plot of Figure 4 gives the strong suggestion that the presence of either unsaturation or a larger-than-third-row atom enhances the quenching, presumably by chemical interaction, since all such neutrals except N_2 and CH_3Br lie substantially above the excellent saturated-molecule trend line.

Equilibration vs. Energy-Flow Quenching. A principal issue in interpreting collisional energy-transfer results in both neutral and ionic systems has been whether energy randomization is complete among the degrees of freedom (or at least some of the degrees of freedom) of the collision complex or whether alternatively the collision duration is too brief for energy equilibration, leading to dominance of the collision duration or the intimacy of the collision in governing the extent of energy transfer. The literature has offered evidence for both types of behavior, and it seems likely that both situations can arise. In the present case, the evidence favors collision-duration limitation and is opposed to energy equilibration.

Evidence on this question is of two kinds. A property of the neutral (mass, usually) can be varied which changes the lifetime of the postulated collision complex without changing the energy partitioning in the equilibrated complex. Thus Miasek and Harrison[4] looking at $C_5H_9^+$ quenching found little variation in quenching efficiency for the rare gases and considered this to indicate energy equilibration. On the other hand, Ferguson et

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(24) Actually the equality of contact time is more fundamental: since the ion–neutral interaction potential well is isotope-independent, Boltzmann statistics predict that the probability of the ion and neutral being found in the potential well is also isotope-independent.

Table III

neutral	full equil collision no.	obsd	neutral	full equil collision no.	obsd
He	37	150	H_2	20	160
Ne	45	100	D_2	20	93
Ar	55	77	CH_4	8	40
Kr	90	30	C_4H_{10}	2.5	13

al.[1] in NO^+ and $O_2{}^+$ find a substantial variation for the rare gases, indicating dominance of the rate of energy flow.

The second line of evidence is the actual amount of energy transferred in each collision: theory, for instance RRKM theory,[25] or the simplified transitional-mode theory,[26] makes specific predictions of the energy partitioning in each collision. In neutral quenching studies, the amount of energy transferred is generally considerably less than the full-equilibration prediction.[27]

The full-equilibration model assumes that the collision complex has time to distribute energy statistically among all internal degrees of freedom and that the equilibrated complex dissociates unimolecularly. Klots[28] has given expressions for the energy carried off by each departing fragment in terms of the equilibration temperature. These expressions are relatively straightforward for quenching by monatomic gases, where kT^* of energy is partitioned into product translation. For more complex quench gases, the participation of rotational degrees of freedom is less easily assessed, but at least approximate values can be given. Polyatomic quench gases of size similar to the excited ion are a particularly simple case where one would expect full-equilibration quenching to remove about half the energy on each collision. A few estimates of full-equilibration collision numbers are compared with our results in Table III. In general the observed quenching is substantially less efficient, but in the heavy rare-gas cases, it becomes comparable.

All indications are that bromobenzene ion quenching is usually limited by the rate of energy flow in the complex. First, the variation among rare gases is substantial, with the heavier atoms (presumably having longer and stronger collisions) being more efficient. Second, the isotope effects for H_2/D_2 and $^3He/^4He$ are as expected for the collision-duration model. Third, for most quench gases, the energy transferred per collision is much less than that predicted on the basis of full equilibration of the collision complex. Our view is that the present data set reflects energy-flow limiting of the quenching efficiency but that quenching in ionic systems is efficient enough that an approach to the saturation situation of full equilibration is not unusual.

In Figure 4 the data are plotted in a way that should roughly reflect the variation in energy flow: The x-axis variable is taken as the product of the square root of reduced mass (reflecting the expected variation in collision duration) and the number of atoms (reflecting the neutral heat capacity). The saturated, uncomplicated molecules (first group in Table I) are seen to give an excellent correlation of quenching efficiency against this variable. The line shown corresponds to a fitting equation

$$Z = 270[N(M_r)^{1/2}]^{-0.68}$$

where N is the number of atoms in the neutral and M_r is the reduced mass. A linear relation between $1/Z$ and $N(M_r)^{1/2}$ also gives a reasonable fit to the data. Out of 18 neutrals only H_2O lies far from the line. While this is only a crude approximation to a true energy-flow model, the correlation suggests some promise for this approach. (While it seems particularly good, the parameter $N(M_r)^{1/2}$ is not unique: Other parameters, such as $F\alpha$, where F is the number of neutral degrees of freedom and α is the polarizability, can be given which yield approximately linear correlations, as long as the neutral size and heat capacity are both taken into account.) It seems very likely that H_2O has its quenching efficiency enhanced by a strong specific chemical interaction.

Table IV. Energy Removed on First Collision (cm^{-1})

	present results	KR[a]	RBP[b]	NBDS[c]	HTW[d]	JB[e]	BB[f]
He	250	280	115	70	75		125
Ne	460	460	175		84		
Ar	590	670	280		130		
Kr	1300	840	240		130		
Xe	1600		210		140		
H_2	280	280–600	150	70	92		
N_2	650	800	245	190	130	385	
O_2	1470		275				
CO	1240		305		160		
CO_2	2400	~1400	425	550	280		
H_2O	4500		420		480		
CH_4	1140	~1400	315		260	630	
C_2H_4	3400				400		
C_2H_6	1860				380		2000[g]
C_4H_{10}	2400		705		640		2600
C_5H_{12}				1280			1100
CH_3Cl	1620	>2500			390		
CH_3Br	1500				440		

[a] Reference 30. [b] Reference 31. [c] References 26, 32, 33. [d] Reference 34. [e] Reference 7. [f] Reference 8a. Barfknecht and Brauman report these to be the average energies lost per collision, which would presumably be somewhat lower than the comparable values for energy lost on first collision, but they also state their belief that their numbers are good estimates of the first-collision energy loss values. [g] C_3H_8.

B. Comparison with Other Results. Comparisons with different experiments are hard because of differences in donor molecule properties, level of internal energy, extent of averaging or biasing in the range of internal energies, measuring method, and data treatment. These problems are severe in comparing absolute quenching rates, as we do in the first section below. Comparisons involving relative quenching efficiencies, as in the second section below, are more tractable, since many uncertainties cancel out, but they are also less informative.

Absolute Values. Several energy-transfer studies involving neutral molecules[27,29] are of interest, involving molecules comparable in size and internal energy level to the excited bromobenzene ions of our work. Table IV makes some comparisons in as nearly uniform a way as we can achieve. Our results have been tabulated in terms of the energy calculated to be transferred on the *first* collision after laser excitation, assuming that the ion energy declines exponentially with the number of collisions. The study by Kohlmaier and Rabinovitch[30] (KR) of the chemically activated *sec*-butyl radical should be a good comparison for these first-collision numbers, since their molecules have comparable excess energy (15 000 cm^{-1}) and become quenched when they have lost only a small amount of energy. Thus only the high internal-energy regime is sampled. Rossi, Pladziewicz, and Barker's study[31] of laser activated azulene is also reasonably comparable. While they tabulate "average" energy removal per collision, they report exponential energy decay for the molecules, and their expression $\Delta E = \beta + \gamma E$ gives the energy removal on a single collision at, for instance, 17 500 cm^{-1}. The quenching of vibrationally excited, electronically excited β-naphthylamine, studied by Neporent,[32] by Boudart and Dubois,[33] and by Stevens[26] (NBDS), is more problematic, since the energy regime is lower (3200–10200 cm^{-1}) and the quenching efficiency is an average over an energy range. Hippler, Troe, and Wendelken's study[34]

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Table V. Relative Quenching Efficiencies

	present results	Miasek and Harrison[a]	Anicich and Bowers[b]	Ferguson et al.[c]
He	0.38	0.48	0.13	<0.0014
Ne	0.70	0.36	0.87	<0.014
Ar	0.91	0.62	1.07	0.59
Kr	2.3	0.52	1.4	6.1
Xe	2.9		1.3	
H_2	0.43	1.14		0.70
D_2	0.75	1.09		0.25
N_2	(1)	(1)	(1)	(1)
CO	1.8	0.95		20
CO_2	3.9	1.8		49
CH_4	1.8	2.7		220
CH_3F	2.4	2.0		
C_2H_6	5.6	4.8		
C_2H_6	2.9	4.8		

[a] Reference 4. [b] Reference 5. [c] Reference 1.

(HTW) of highly (52000 cm^{-1}) laser excited C_7H_8 is quite comparable if, as they report, the energy removed per collision is constant over the relevant energy range. Recently, Barfknecht and Brauman[8a] (BB) used a visible/IR two-laser technique, which appears to be quite comparable to the present one-laser two-photon technique, to measure quenching of bromo(trifluoromethyl)-benzene cation by a few gases. Finally, Jasinski and Brauman[7] (JB) report absolute energy-removal values for several gases with CF_3O^-, which are properly only upper-limit values but are interesting for comparison.

It is seen that the KR results look quite similar to ours in magnitude, and in the range and character of the variation with quenching neutral. This is also true for a number of other chemically activated neutral quenching studies.[27] NBDS gives numbers which appear quite consistently about a factor of 4 less than ours, but with similar quench-gas dependences. RPB correlates less well with our trends, showing less increase in efficiency for more complex quench neutrals, as well as showing smaller efficiencies even for small neutrals. HTW are rather similar to RPB, but they are mostly even lower in efficiency. The values of BB are quite similar to ours and would be even closer if they had been adjusted to estimate the energy removed on the first collision, rather than the average energy removed. This similarity is not surprising, since BB made their measurements on an ion similar to the bromobenzene ion, using a technique in many respects similar to ours. They made a comparison of their results with a full equilibration model, which predicted much more than the observed energy transfer, and with a more sophisticated elaboration of the collision-duration model by Forst and Bhattacharjee,[35] which predicted the energy transfer poorly. Their conclusion, similar to ours, was that neither of these types of model is successful in their system. The upper limits of JB are about half our values, but this could well be attributed to a lower ion-energy regime (their ion energy being unknown) and to the smaller ion.

Relative Values. Only a few studies of polyatomic ion quenching by a range of neutral quenchers have been reported, and these have been relative, not absolute, results (see Table V). Miasek and Harrison[4] looked at the quenching of $C_5H_9^+$ reactively formed with an amount of internal energy which was not confidently known. Their results are relevant for comparison with our results, since the excess internal energy is substantial, and substantial energy must be removed by collisions to have an observable quenching effect. Some of their relative efficiencies are shown in Table V. These data show a similar range of variation to our results, although the individual correlations for the same neutral are rather erratic, and the high H_2 value and the low variation among the rare gases are in contrast to our results.

Anicich and Bowers,[5] studying the collisional stabilization of dimer ion complexes in CH_2F_2 and C_6H_6, found substantial (factor of three) increases in stabilization efficiency going from He to heavy rare gases (Table V) and argued for a collision-duration model in these cases. On the other hand, in the collisional stabilization of $(CH_3)_3N$ dimer ion complexes studied by Bass et al.,[9] little variation in efficiency was found among a number of nonpolar quenchers, all of which quench at ~0.4 times the efficiency of the parent neutral; modest increases were observed for polar quenchers. It was concluded that a collision-duration model does not describe this system. These dimer-stabilization studies are less directly comparable to our results, since the removal of only a small amount of energy suffices to stabilize the complex, and it is quite likely that all quench gases will be quite efficient. In probing the mechanism of quenching, it is preferable to work with systems with wider variations in efficiency.

Ferguson et al.[1] have studied collisional removal of a single quantum of vibration from NO^+ and O_2^+ (see Table V) and find dramatic variations in efficiency for different quench gases, which they interpret in terms of a collision-duration (or "complex" duration) model. The range of variation is extremely large. These studies may be more relevant for comparison with our results than the dimer-stabilization studies, since the removal of the rather high-energy vibrational quantum of the diatomic ion may be a reasonable model for the quenching of the vibrations of the fairly rigid bromobenzene ion. The trends are generally similar, but much more pronounced in the diatomic ion cases.

Conclusion

This study represents the first polyatomic ion quenching study with a broad spread of quenching partners by a technique giving a measure of the absolute energy transferred per collision. The absolute quenching efficiency for a given quench partner is higher by a factor of 2 to 4 than has been reported in several comparable optically excited neutral quenching studies, but it is similar to the values reported for a number of chemically activated neutral systems. Thus the question of whether the charge enhances the quenching depends on what is taken to be typical behavior for neutrals, but it would be reasonable to attribute at least some enhancement to the presence of the ion–neutral electrostatic interaction.

The trends observed for the series of different neutral partners are not surprising, showing the same sorts of dependence on mass and heat capacity as have been found in other neutral and ion systems. A number of observations and arguments point to this being a system in which the quenching is limited by the rate of energy flow within the collision complex, putting this system in contrast to a few systems, including some ion systems, where equilibration appears to be approached in the complex. Particularly clear in this study is the extraordinarily close correlation of the quenching rate for the subset of saturated quench gases with the parameter $N(M_r)^{1/2}$, taking into account both the duration of the collision and the heat capacity of the neutral. Also clear is the substantial enhancement of the quenching for a number of unsaturated and heavy-atom gases for which chemical interaction with bromobenzene ions could be expected.

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