

THE JOURNAL OF PHYSICAL CHEMISTRY

Registered in U. S. Patent Office © Copyright, 1971, by the American Chemical Society

VOLUME 75, NUMBER 6 MARCH 18, 1971

Some Relative Total Scattering Cross Sections for Homologous Series of Polar and Nonpolar Molecules^{1a}

by W. H. Duewer,^{1b} G. J. Williams, C. F. Aten,^{1c} and B. S. Rabinovitch*

Department of Chemistry, University of Washington, Seattle, Washington 98105 (Received September 10, 1970)

Publication costs assisted by the U. S. Air Force Office of Scientific Research

Relative total scattering cross sections were measured for several homologous series of gases using low-resolution thermal crossed molecular beams. The experimental cross sections were compared with cross sections calculated on various models and with energy-transfer cross sections obtained by other workers from the study of unimolecular methyl isocyanide isomerization. The experimental values for polar gases were well reproduced by calculations using a treatment developed by Cross and Gordon. Those for other gases were in reasonable agreement with conventionally calculated scattering cross sections.

Introduction

The low-pressure thermal unimolecular isomerization of methyl isocyanide (A) has provided activation-deactivation (energy transfer) cross sections for a large number of inert bath gases (M).² These cross sections may be interpreted as the product of a collisional efficiency, β_e , and a gas kinetic cross section, πs_{AM}^2 . The gas kinetic cross sections for nonpolar bath molecules were calculated with the use of Lennard-Jones potential constants derived from viscosity measurements of the pure gases; standard mixing rules were used.³ Estimates of potential parameters were employed when experimental values were not available. Among the bath molecules studied were homologous series of similar gases,^{4,5} *n*-alkanes, 1-alkenes, 1-alkynes, terminal nitriles, and *n*-fluoroalkanes. The potential constants used for the larger gases in each series were usually based on estimates from the known constants of the smaller members.

For the series of strongly dipolar terminal nitriles, a dipole orientation effect was suggested⁶ as the explanation for an apparent near-equivalence of kinetic cross sections measured for acetonitrile and propionitrile; the method of Monchick and Mason⁶ was used to treat the dipolar interactions. This involves approximations,

pointed out by the original authors, which may introduce a systematic error into the cross sections; this treatment used the Stockmayer potential and simple geometrical weighting of dipole orientations; as a result, the cross sections are independent of molecular rotations. A more recent treatment⁷ of the interactions of dipoles based on the Born approximation shows a strong dependence of calculated collision cross sections

(1) (a) This work was supported by the U. S. Air Force Office of Scientific Research (SRC), Contract No. F44620-70-C-0012; (b) NSF predoctoral fellow 1967-1970; (c) Sabbatical visitor.

(2) S. C. Chan, B. S. Rabinovitch, J. T. Bryant, L. D. Spicer, T. Fujimoto, Y. N. Lin, and S. P. Pavlou, *J. Phys. Chem.*, **74**, 3160 (1970).

(3) J. O. Hirschfelder, C. F. Curtiss, and R. B. Bird, "Molecular Theory of Gases and Liquids," Wiley, New York, N. Y., 1954, Chapter 8.

(4) Y. N. Lin, S. C. Chan, and B. S. Rabinovitch, *J. Phys. Chem.*, **72**, 1932 (1968).

(5) S. C. Chan, J. T. Bryant, L. D. Spicer, and B. S. Rabinovitch, *ibid.*, **74**, 2058 (1970).

(6) (a) L. Monchick and E. A. Mason, *J. Chem. Phys.*, **35**, 1676 (1961); (b) E. A. Mason and L. Monchick, *ibid.*, **36**, 2746 (1962).

(7) (a) R. J. Cross and R. G. Gordon, *ibid.*, **45**, 3571 (1966); (b) since this paper was written, a recent treatment by H. Rabbitz and R. G. Gordon [*J. Chem. Phys.*, **53**, 1815, 1831 (1970)] gives the magnitude of some additional terms. Inclusion of their terms may improve the agreement between calculation and experiment for most of the gases in this study.

on the rotational periods of colliding dipolar molecules. This treatment has been moderately successful in predicting total scattering cross sections in high-resolution beam experiments.⁸

In order to investigate further the cross-sectional behavior of the nitrile series, we have made total scattering molecular beam measurements on acetonitrile-nitrile collision pairs. The beam apparatus which was available was not originally designed for total scattering measurements. Its chief failings were low resolution and lack of velocity-selection. All of the measured cross sections are thermal average values. Because of the difficulties introduced into the interpretation of the data by the low resolution, measurements were made on acetonitrile-alkyne collision pairs which, by comparison with the acetonitrile-nitrile scattering, specifically isolates the contributions of dipole-dipole interactions in the latter pair. Other suitable comparison series were also studied.

Experimental Section

A diagram of the apparatus is given in Figure 1. The slit dimensions, pressure measuring devices, and typical operating conditions are collected in Table I.

Table I: Apparatus Parameters

	Dimensions, cm	Pumping	Pressure, Torr Beams off	Pressure, Torr Beams on
S ₁	0.010 × 0.5			
S ₂	0.032 × 0.5			
P ₁ ^{a,b}		2-in. oil diffusion	<10 ⁻⁶	10 ⁻⁶
S ₃	0.015 × 0.5			
S ₄	0.15 × 0.5			
P ₂ ^b		6-in. oil diffusion	<10 ⁻⁷	~10 ⁻⁵
S ₅	0.10 × 0.5			
P ₃ ^b		2-in. oil diffusion	<10 ⁻⁶	5 × 10 ⁻⁶
S ₆	0.22 × 0.5			
P ₄		500 l. sec ⁻¹ sputter-ion	<10 ⁻⁸	5 × 10 ⁻⁸
S ₇	0.62 diameter			

^a A liquid nitrogen cold finger extended into the chamber.

^b All oil diffusion pumps were trapped by a liquid nitrogen cryobaffle adjacent to the apparatus.

The detector was an EAI Quad 200 mass filter equipped with an axial beam ionizer. The ionization efficiency was estimated to be $\lesssim 10^{-4}$.

The parent beam was modulated at 200 Hz by an American Time Products tuning fork chopper, C₁. The secondary beam could be similarly modulated at 223 Hz, C₂.

The primary beam intensity was measured by detecting the 200-Hz component of a suitable peak in the

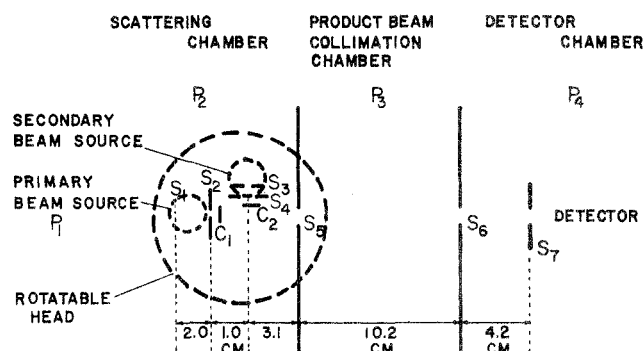


Figure 1. Schematic of the apparatus.

mass spectrum of the parent beam molecule with a PAR 121C lock-in amplifier. The scattered intensity was taken as the 223-Hz component of the same peak. A peak was suitable if it was prominent in the spectrum of the primary beam molecule, absent from the spectrum of the scattering gas, and weak in the general background spectrum. It is obvious that there were no suitable peaks available for the study of the scattering of a gas by itself.

Experimental Measurements and Treatment of the Data

The observed total scattering cross section, Q_{obsd} , is defined by the relation

$$Q_{\text{obsd}} = \ln(I_0/I)/n_j L \quad (1)$$

where I_0 is the intensity of the primary beam in the absence of scattering, I is the intensity of the primary beam after scattering, n_j is the density of scattering particles in the secondary beam, and L is the length of the scattering zone. Since, for effusive flow from a long slit collimated at a distance from the zone of interaction, n_j and L are inversely related, they were evaluated together. Assuming Knudsen flow

$$n_j L = N_0 L_0 F / 4$$

where N_0 is the density of particles behind the source slit, L_0 is the width of the source slit (0.015 cm), and the collimation factor F is given by⁹

$$F = \int_{-a}^{+a} \cos \theta \, d\theta / \int_{-\pi/2}^{+\pi/2} \cos \theta \, d\theta = 0.20 \pm 0.08$$

where $2a$ is the angular width of the secondary beam collimator; the rather crude error limits for F were estimated from experimental measurements and apparatus features. All of the above factors were constants of the apparatus except for N_0 which was made a constant of the experiment; thus $n_j L = KN_0$, where $K = 7.5 (\pm 3.0) \times 10^{-4}$ cm and N_0 is calculated from P_0 , the pressure behind the secondary beam slit. P_0 was mea-

(8) R. J. Cross, E. A. Gislason, and D. R. Herschbach, *J. Chem. Phys.*, **45**, 3582 (1966).

(9) For a more complete discussion of these matters see W. H. Duewer, Ph.D. Thesis, University of Washington (1970).

sured on a thermocouple gauge that had been calibrated by expansion of the gases involved between standard volumes; actually, absolute calibration was not required for the present relative measurements. I , the intensity after scattering, was proportional to the maximum amplitude of the 200 cycle-chopped primary beam, measured with the secondary beam on; the intensity before scattering, I_0 , was taken to be equal to the sum of I and I_{sc} , the total intensity of molecules scattered out of the beam. For the purpose of calculating Q_{obsd} , I_{sc} was taken to be proportional to the amplitude of the 223-cycle signal at its maximum; this signal was 180° out of phase with respect to the chopper. In the calculation, the ratio of true molecule density to signal intensity was assumed to be the same for both frequencies. This should introduce only minor errors into the absolute cross section, already uncertain by $\sim 40\%$ due to uncertainty in F . Also, since I_{sc} was always less than 4.5% of I , then $I_0/I \simeq 1$, and since for small x , $\ln(1+x) \simeq x$, the relative cross sections should be virtually unaffected by a failure of this assumption. The chopper characteristics were not altered during the course of the investigation.

The observed collision diameter is defined by $\sigma_{obsd} = (Q_{obsd}/\pi)^{1/2}$. The experimental quantity Q_{obsd} (eq 1) may be equated simply to calculated values based on the intermolecular potential only if the scattering beam particles are stationary and if the primary beam is velocity selected, say at some reference velocity, v_0 . Since the scattering molecules are not stationary, the relative velocity, g , differs from the primary beam velocity and the calculated collision rate is too small if based on the primary beam velocity. The cross section calculated from the attenuation is too large by a factor of (g/v_0) , for a velocity-independent (*i.e.*, hard sphere) cross section; also, the true cross section is velocity dependent for potentials other than hard sphere. For thermal beams, it is necessary to average over the distribution of velocities.

Berkling, *et al.*,¹⁰ have given functions which correct for these effects. Since our experiments were carried out at low resolution, it was necessary⁸ to use the classical relation for the dependence of total cross section on the relative velocity,⁹ $Q_c \propto g^{-2/3}$. In Berkling's notation, we used a $G_{b'o}(4, y)$ correction for thermal crossed beams, a density-sensitive detector, and spherical molecules. The argument y is the ratio of the most probable velocity in the primary beam to that of the secondary beam. The velocity-corrected cross sections are given by

$$Q(v) = Q_{obsd}/G_{b'o}(4, y) \quad (2)$$

This correction refers the experimental cross sections to the most probable velocity of the primary beam. The velocity-corrected collision diameters are designated as $\sigma_{obsd}(v)$.

Calculated Collision Properties. The energy transfer collision diameters obtained from isomerization studies have been compared with those calculated from viscosity measurements with use of Lennard-Jones or Stockmayer potentials and the relation, $s_{ij}^2 = \sigma_{ij}^2 [\Omega^{*(2,2)}(\epsilon_{ij}/T, \delta_{max})]$ where σ_{ij} is the Lennard-Jones parameter and $\Omega^{*(2,2)}(\epsilon_{ij}/T, \delta_{max})$ is tabulated for both nonpolar collisions⁸ ($\delta_{max} = 0$), and for polar-polar collisions⁶ ($\delta_{max} > 0$). Molecular beam scattering cross sections for Lennard-Jones gases have usually been calculated by the use of the relation

$$Q_{ij} = 8.08(C/g)^{2/3} \quad (3)$$

where C is the constant multiplying the r^{-6} term in the potential ($4\epsilon_{ij}\sigma_{ij}^6$, in the Lennard-Jones expression). In general, for molecular beam scattering, C has not been taken from viscosity-derived potentials but has been calculated from the molecular polarizability and dipole-induced dipole effects. C is taken to be equal to the sum of a dispersion term and an induction term. The dispersion term is given by the Slater-Kirkwood approximation and the induction term by the Debye relation. That is

$$C = C_{disp} + C_{ind} \quad (4)$$

where

$$C_{disp} = \frac{25.2 \times 10^{-24} \alpha_i \alpha_j}{[(\alpha_i/N_i)^{1/2} + (\alpha_j/N_j)^{1/2}]}$$

and

$$C_{ind} = \alpha_i \mu_j^2 + \alpha_j \mu_i^2$$

the α 's are the polarizabilities, the N 's are the number of outer shell electrons, and the μ 's the dipole moments of the molecules.

Dipole-dipole forces have been treated by several general approaches. In the Keesom-Linder approximation,¹¹ the dipole-dipole orientations are given their Boltzmann weightings, and the potential is averaged over the orientations. This approach was used by Bernstein, Rothe, and Schumacher¹² (BRS) in the treatment of beam scattering. A second approach¹³ invokes the sudden approximation and yields very large cross sections.⁷ A third treatment by Cross and Gordon⁷ used the Born approximation in first-order perturbation theory and yields cross sections smaller than those calculated from the sudden approximation, but usually larger than those calculated using the Keesom-

(10) K. Berkling, R. Helbing, K. Kramer, H. Pauly, C. Schlier, and P. Toschek, *Z. Phys.*, **166**, 406 (1962).

(11) W. Keesom, *ibid.*, **22**, 129 (1921); B. Linder, *J. Chem. Phys.*, **44**, 265 (1966).

(12) (a) E. W. Rothe and R. B. Bernstein, *ibid.*, **31**, 1619 (1959); (b) H. Schumacher, R. B. Bernstein, and E. W. Rothe, *ibid.*, **33**, 584 (1960).

(13) H. G. Bennewitz, H. H. Kramer, U. Paul, and J. P. Toennies, *Z. Phys.*, **177**, 84 (1964); H. H. Kramer and R. B. Bernstein, *J. Chem. Phys.*, **44**, 4473 (1966).

Linder approximation; these cross sections are strongly dependent on the rotational periods of the colliding molecules. The Keesom-Linder approximation is a choice based on convenience and previous use. It is not a part of modern scattering theory, although second-order perturbation theory gives rise to terms which have a weaker dependence on rotational resonance and somewhat resemble the results of the Keesom-Linder expression.^{7b}

The method of Bernstein and Rothe^{12a} for treating nonpolar collision pairs has given fair agreement with experiment for collisions between alkali metals and a variety of gases; the agreement is best for simple molecules. The treatments of dipole-dipole interactions involving preaveraging have given fair agreement with molecular beam experiments when the cross-section contribution due to dipole-dipole interactions was comparable to that due to dispersion forces.^{8,12} The treatment of Cross and Gordon has given better results when the cross sections calculated from dipole-dipole interactions is much larger than that due to dispersion forces.⁷

In this work, scattering collision diameters have been calculated with use of the Keesom-Linder approximation^{12b} and by using the method of Cross and Gordon⁷ as applied to classical dipoles by Cross, Gislason, and Herschbach⁸ (CGH). Asymmetric top molecules were approximated as linear molecules whose rotational moment of inertia was equal to the mean moment about the axes perpendicular to the dipole. Where microwave spectra were available, the rotational moments were taken from these; where no spectra were available, the moments were approximated as for the fully extended configuration, with all masses concentrated at points along the molecular axis. Fortunately, the instances where these approximations are worst are the cases where errors in moments of inertia have the least effect on the calculated values.

Collision diameters have also been calculated from the viscosity-derived potentials in two ways. The hard-sphere diameters that would yield equivalent viscosities have been computed, as in the unimolecular reaction energy-transfer work.² Also, collision diameters have been calculated from the attractive potential

$$C = -[4\epsilon_{ij}\sigma_{ij}^6 + 2/3\mu_i^2\mu_j^2/kT] \quad (5)$$

as in the treatment of BRS, but using viscosity-derived potential parameters. These parameters have also been calculated for collisions at 280°, the temperature of the energy-transfer work.

Cross sections calculated from the attractive potentials are the normal ones for comparing with molecular beam scattering results. Hard-sphere viscosity-related diameters are included for comparison with the energy-transfer conditions; they can reveal the effect of heavily weighting the large angle scattering (weighting of $\Omega^{*(2,2)}$ by $\sin^2 \phi_{cm}$, where $cm \equiv$ center-of-mass coordi-

nate system). The weighting given to the large angle scattering, which results from the low resolution of our apparatus, while not as great as in viscosity measurements is greater than in high-resolution scattering experiments. The parameters used in calculating the cross sections are given in Table II.

Table II: Some Molecular Parameters

	$\sigma_{ii},^a$ 10 ⁻⁸ cm	$\epsilon_{ii}/k,^a$ °K	$\alpha_i,^a$ 10 ⁻²⁴ cm ³	$\mu_i,^a$ D	I_i 10 ⁻⁴⁰ g cm ²
CH ₃ CN	4.47	380	4.27	3.97	90.9 ^c
CH ₃ NC	4.47	380	4.47	3.80	83.2 ^c
C ₂ H ₆	5.06	254	6.29	0.0	
C ₂ H ₂	4.22	185	3.33	0.0	
C ₂ H ₄	4.74	261	5.0	0.75	95 ^d
C ₂ H ₆	5.25	310	6.7	0.81	200 ^e
C ₂ H ₈	5.75	310 ^b	8.5	0.86	390 ^e
C ₂ H ₁₀	6.25	310	10.5	0.88	750 ^e
C ₂ H ₁₂	6.75	310	12.4	0.87	1250 ^e
C ₂ H ₁₄	7.25	310	14.3	0.87	1800 ^e
C ₂ H ₁₆	7.75	310	16.2	0.87	2600 ^e
HCN	3.93	320	2.59	2.95	18.9 ^f
CD ₃ CN	4.47	380	4.27	3.97	115 ^g
C ₂ H ₅ CN	5.00	380 ^b	6.07	4.03	198 ^h
C ₂ H ₇ CN	5.50	380	7.8	4.07	390 ⁱ
C ₂ H ₉ CN	6.00	380	9.6	4.12	750 ^j
C ₂ H ₁₁ CN	6.50	380	11.5	4.2	1250 ^j
C ₂ H ₁₃ CN	7.00	380	13.4	4.2	1800 ^j
C ₂ H ₁₅ CN	7.50	380	15.4	4.2	2600 ^j
Ne	2.79	36	0.392	0.0	
CD ₄	3.8	144	2.6	0.0	
NH ₃	3.15	358	2.26	1.47	4.37 ^{f,k}
ND ₃	3.15	358	2.26	1.47	8.86 ^{f,k}
N ₂	3.68	92	1.76	0.0	
C ₂ H ₅ OH	4.50	300	4.9	1.69	140 ^l
C ₂ H ₁₂	5.77	325	9.95	0.0	

^a See ref 2 for sources. ^b An alternative choice for ϵ_{ii} for higher homologs, which increases with boiling point, was also tested. It led to no significant change in the behavior of Figures 2-5; hence the values of ref 2 were adopted. ^c H. Ring, H. Edwards, M. Kessler, and W. Gordy, *Phys. Rev.*, **72**, 1262L (1947). ^d R. Trambarulo and W. Gordy, *J. Chem. Phys.*, **18**, 1613 (1950). ^e Estimated from the moments of the similar nitrile. ^f G. Herzberg, "Molecular Spectra and Molecular Structure II Infrared and Raman Spectra of Polyatomic Molecules," D. Van Nostrand, Princeton, N. J., 1945. ^g Calculated from the known geometry of CH₃CN. ^h R. G. Lerner and B. P. Dailey, *J. Chem. Phys.*, **26**, 678 (1957). ⁱ E. Hirota, *ibid.*, **37**, 2918 (1962). ^j Estimated as discussed in the text. ^k The more nearly resonant rotation about the dipole axis was used. ^l B. Bak, E. S. Knudsen, and E. Madsen, *Phys. Rev.*, **75**, 1622L (1949).

Correction for Finite Resolution. The cross sections calculated from eq 3 are those that would be measured on a high-resolution apparatus, since there exists a limiting cm angle, α_0 , within which the cross section is nearly independent of angle¹⁴

(14) H. Pauly and J. P. Toennies, *Advan. At. Mol. Phys.*, **1**, 201 (1965).

$$\alpha_0 = \frac{h}{2M_i v_i} (\pi/Q_{\text{tot}})^{1/2} \quad (6)$$

where M_i is the mass of the primary beam molecule, v_i is its velocity, and Q_{tot} is the total cross section. For the systems studied here, α_0 ranges between 0.01 and 0.2°, whereas the angular resolution of the apparatus was 0.75° (lab, *i.e.*, laboratory coordinates), or 1–3° (cm).¹⁵ Experimentally, cross sections measured on an apparatus with angular resolution equal to α_0 are low by 5–10%.¹⁴ It was necessary to correct for the finite resolution of the apparatus.⁹

The error in our absolute measurements is as much as a factor of four, although the effect on the relative cross sections is much smaller, 10–20%, if the correction is made using the expressions given by CGH for low-resolution experiments. These corrections take the form

$$Q_c(\theta_R) = Q_c(0)(A + B/\rho^{1/3}) \quad (7)$$

where $Q_c(\theta_R)$ is the cross section calculated at the experimental resolution, $Q_c(0)$ is the cross section calculated for infinite resolution, A and B are constants given by the form of the potential, and ρ is the resolution parameter given by

$$\rho = M_i v_i Q_c(0)^{1/2} W / l h$$

where M_i is the mass and v_i the velocity of the primary beam particle (taken as the most probable velocity),¹⁶ h is Planck's constant, W is the width of the beam at the detector, and l is the distance from the source to the detector. For scattering from an r^{-6} potential, $A = 0.0814$ and $B = 0.5804$. For scattering resulting from dipole-dipole interactions calculated on the Born model,⁸ $A = -0.0270$ and $B = 0.6018$. The Keesom-Linder approximation converts the dipole-dipole interaction to an r^{-6} form. Relative collision diameters calculated on this basis are given in the tables as $\sigma_c(\theta)$. It should be noted that these approximate corrections were developed⁹ for experiments of better resolution than the present ones and may be less accurate as applied here.

Results

Table III gives collision diameters for the pair ace-

Table III: Magnitudes of CH₃CN–CD₃CN Collision Diameters (Å)

σ_{obsd}^a	$\sigma_{\text{obsd}}(v)^a$	σ_{CGH}^b	σ_{BRS}^b	$\sigma_{\text{BRS}}^{b,c}$	σ_η^d
9.1	8.0	(40.4) 16.6	(26.9) 13.9	(28.1) 14.5	7.21

^a The absolute value of the experimental collision diameter has order-of-magnitude significance only. ^b The parenthetic value is the cross section calculated for high resolution; the lower value includes the finite resolution correction. ^c BRS treatment using viscosity-derived long-range potential. ^d Hard-sphere equivalent viscosity-based collision diameter.

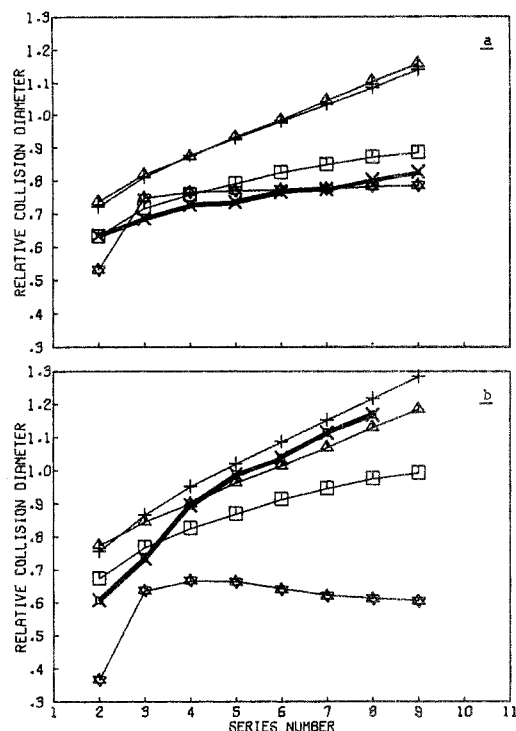


Figure 2. (a) Relative collision diameter vs. series number for the series alkynes vs. CH₃CN at 294°K: ×, scattering collision diameter; Δ, hard-sphere-equivalent viscosity-based collision diameter; +, collision diameter calculated from viscosity based-attractive forces; □, BRS collision diameter; ☆, CGH collision diameter. (b) Relative collision diameter vs. series number for the series alkynes vs. CH₃CN at 554°K: ×, energy transfer collision diameter; Δ, hard-sphere-equivalent viscosity-based collision diameter; +, collision diameter calculated from viscosity-based attractive forces; □, BRS collision diameter; ☆, CGH collision diameter.

tonitrile-*d*₃-acetonitrile. All diameters for other pairs are given relative to the pair, acetonitrile-*d*₃-acetonitrile. Comparisons of the data are presented in Figures 2–8; relative collision diameters of members of a homologous series are plotted against the number of skeletal atoms; collision diameters for molecules in groups of near-equal mass, which were chosen to minimize the effects of approximations in the treatment of the velocity dependence of the collision diameters and the correction for finite resolution, are plotted in order of increasing cross section.

In judging the goodness of fit amongst the curves in each of the figures that follow, it should be borne in mind that it is probably quite reasonable to conceive of small vertical displacements of the experimental curves as might be occasioned by residual errors in the data treatment.

Alkynes–Acetonitrile. Figure 2a shows the experimental relative collision diameters and the calculated

(15) P. Kusch, *J. Chem. Phys.*, **40**, 1 (1964).

(16) Thermal averaging over primary beam velocities of the resolution correction, as opposed to use of the most-probable-velocity correction, had less than a 0.5% effect on the relative collision diameters.

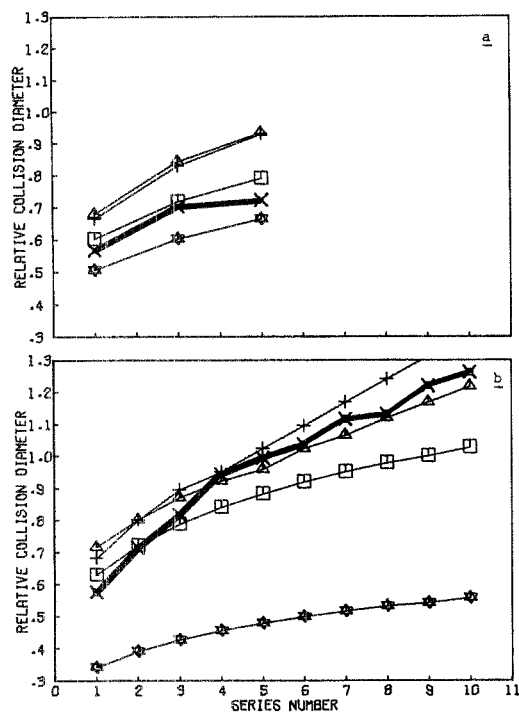


Figure 3. (a) Relative collision diameter *vs.* series number for the series alkanes *vs.* CH_3CN at 294°K. Same symbols as in Figure 2a. (b) Relative collision diameter *vs.* series number for the series alkanes *vs.* CH_3NC at 554°K. Same symbols as in Figure 2b.

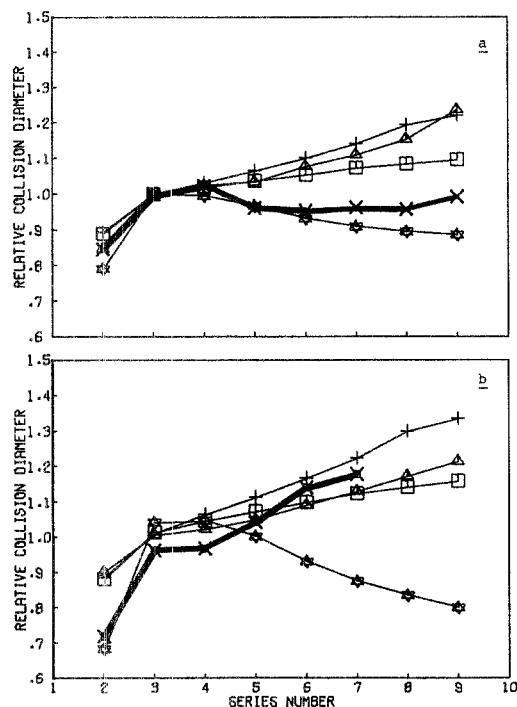


Figure 4. (a) Relative collision diameter *vs.* series number for the series nitriles *vs.* CH_3CN at 294°K. Same symbols as in Figure 2a. (b) Relative collision diameter *vs.* series number for the series nitriles *vs.* CH_3NC at 554°K. Same symbols as in Figure 2b.

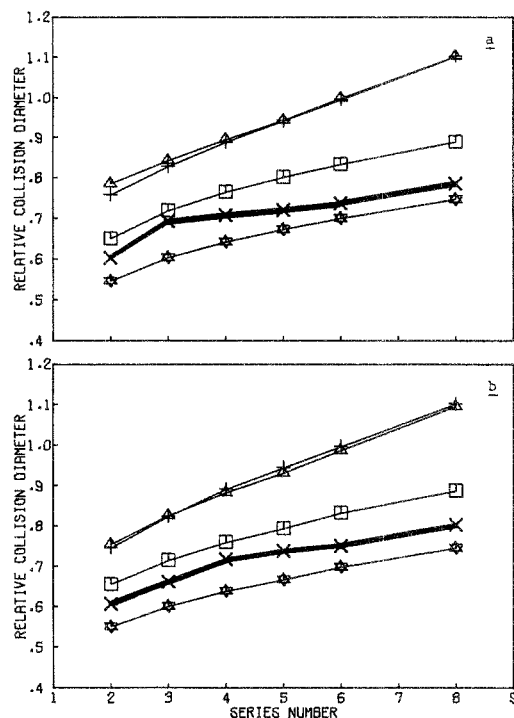


Figure 5. (a) Relative collision diameter *vs.* series number for the series nitriles *vs.* C_3H_8 , at 294°K. Same symbols as in Figure 2a. (b) Relative collision diameter *vs.* series number for the series alkynes *vs.* C_3H_8 at 294°K. Same symbols as in Figure 2b.

resolution-corrected relative collision diameters for alkyne-acetonitrile collisions. The experimental quantities are in better agreement with those calculated from the model of BRS than with that of CGH. The behavior for the smaller molecules suggests that CGH over estimates the contribution of weak dipole-dipole interactions to the cross section. Calculations based on the viscosity-derived potentials do not agree with the experimental diameters in any part of the range.

Figure 2b shows the reported behavior of the alkyne series for energy transfer in CH_3NC isomerization. The agreement with viscosity-derived values is good for all except the smallest alkynes; however, the known collisional inefficiency of the latter,² $\beta < 1$, should cause the energy-transfer cross sections to drop below those based simply on viscosity. As was expected, the models of CGH and BRS do not fit the data.

Alkanes-Acetonitrile. Methane, propane, and pentane were studied in collisions with acetonitrile. The results are seen in Figure 3a. Here the agreement is best with the BRS values. The results from CH_3NC energy-transfer experiments are summarized in Figure 3b; again, the larger molecules, having $\beta = 1$, give good agreement with the viscosity-derived values.

Nitriles-Acetonitrile. The results of the nitrile-acetonitrile scattering experiments are given in Figure 4a. The maximum observed in the experimental diameters at acetonitrile- d_3 and propionitrile is well repro-

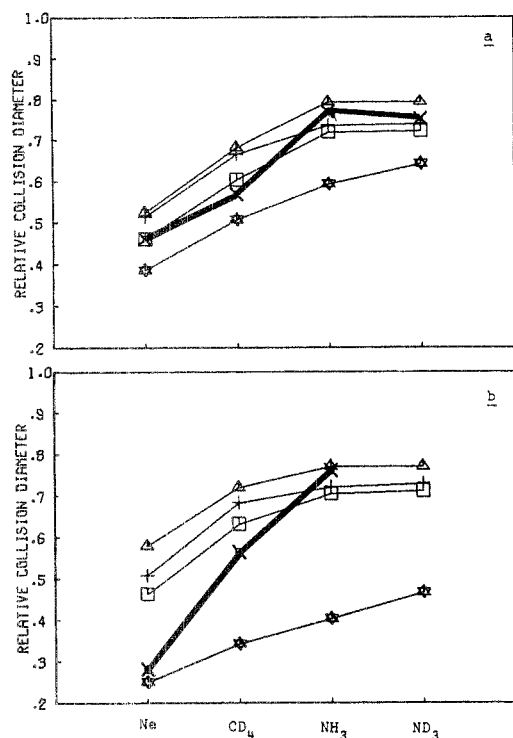


Figure 6. (a) Relative collision diameters for the series of molecules of mass near 20 in collision with CH_3CN at 294°K . Same symbols as in Figure 2a. (b) Relative collision diameters for the series of molecules of mass near 20 in collision with CH_3NC at 554°K . Same symbols as in Figure 2b.

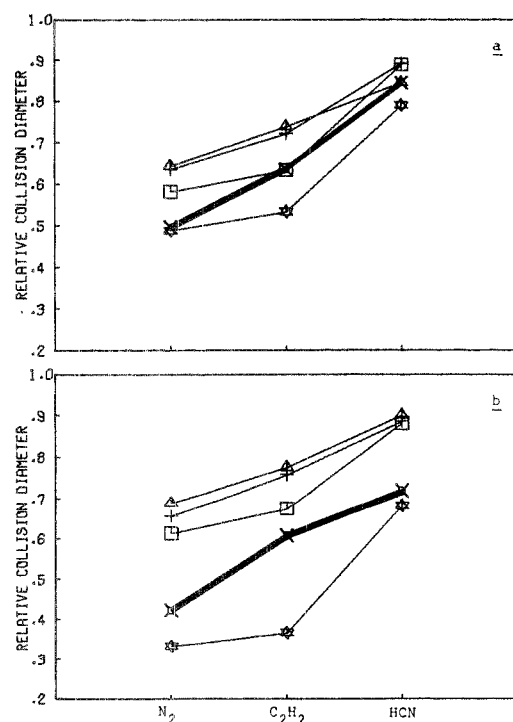


Figure 7. (a) Relative collision diameters for the series of molecules of mass near 28 in collision with CH_3CN at 294°K . Same symbols as in Figure 2a. (b) Relative collision diameters for the series of molecules of mass near 28 in collision with CH_3NC at 554°K . Same symbols as in Figure 2b.

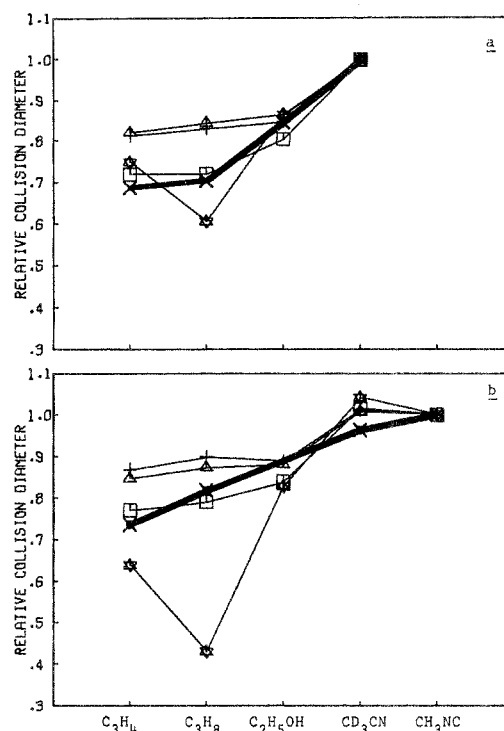


Figure 8. (a) Relative collision diameters for the series of molecules of mass near 42 in collision with CH_3CN at 294°K . Same symbols as in Figure 2a. (b) Relative collision diameters for the series of molecules of mass near 42 in collision with CH_3NC at 554°K . Same symbols as in Figure 2b.

duced by CGH; however, the values for the largest nitriles are not as well reproduced. The other models do not agree as well with experiment. The source of the maximum in the CGH cross sections is near-resonant rotational energy transfer; the model seems to underestimate nonresonant interactions of strong dipoles.

The CH_3NC energy-transfer results are shown in Figure 4b. Here no model fits the data well, although the viscosity-based diameters most nearly fit most of the data. The enhancement of the acetonitrile- d_3 collision diameter is similar to the scattering behavior and suggests a coupling of dipoles near rotational resonances. Vibrational resonance might enter into the explanation of this behavior: although the trideuteration of the d_3 compound substantially destroys any higher frequency vibrational resonances between excited methyl isocyanide and acetonitrile- d_3 , the low-lying bending near-resonances still persist. However, the importance of vibrational resonance in this phenomenon is still not clear.^{2,17}

Alkynes and Nitriles vs. Propane. To verify that the observed qualitative differences between the collisional behavior of the alkyne series (Figure 2a) and the nitrile series (Figure 4a) with a polar collision partner were a result of the dipole-dipole interaction, the behavior of the alkynes (Figure 5a) and nitriles

(17) Y. N. Lin and B. S. Rabinovitch, *J. Phys. Chem.*, **74**, 3151 (1970).

(Figure 5b) in collision with propane, a nonpolar gas of about the same mass and complexity as acetonitrile, was studied. As all of the models predicts, the behavior of the two series was similar, and similar to alkyne-acetonitrile and alkane-acetonitrile scattering. The agreement between experiment and calculation was fair for the relative collision diameters calculated from the BRS and CGH models. Obviously, the treatment of the dipolar interaction affected only the reference collision diameter, acetonitrile- d_3 -acetonitrile, since propane is nonpolar.

Some Molecules of Equal Mass vs. Acetonitrile. The effects of any inadequacy in the handling of the corrections for resolution and for relative motion of the scattering particles are minimized in studies of small series of nearly equimassive molecules.

The molecules Ne, CD₄, NH₃, and ND₃, all near mass 20, were studied in collision with acetonitrile. The results are shown in Figure 6a. The calculated BRS values seem to be in good agreement with the experiment. Figure 6b gives the behavior of the relative collision diameters in energy-transfer (isocyanide isomerization) collisions. Here the apparent collision diameters, which include an inefficiency factor $\beta < 1$, are not expected to agree with any model.

The molecules N₂, C₂H₂, and HCN, all of mass near 27, were studied in acetonitrile scattering experiments. The results are given in Figure 7a. None of the models fit particularly well, although the BRS and CGH models give reasonable fits. Figure 7b shows the isocyanide collision diameters. Again no model agrees well with the experiment. And again, the explanation includes collisional inefficiency effects.

Another series of nearly equimassive molecules was studied, and the acetonitrile scattering results for propyne, propane, ethanol, and acetonitrile- d_3 are given in Figure 8a. The agreement with the calculations from BRS is fairly good. The isocyanide relative collision diameters are given in Figure 8b. All models yield fair agreement with experiment.

Discussion

The acetonitrile scattering behavior of the nitriles and of ethanol is well described by the theory of CGH. However, the dipole contributions to the collision diameters of weakly dipolar molecules with near-resonant rotational periods (*e.g.*, propyne, butyne) is overestimated and the cross sections of strongly dipolar molecules far from rotational resonance (*e.g.*, NH₃, ND₃, and, to a lesser extent, HCN and the largest nitriles) are underestimated. This observation agrees with the findings of CGH, who found that the model gave good results if the contribution to the cross section from the dipolar interaction was significantly greater than that from dispersion forces, but that the Keesom-

Linder approximation gave better results when the contribution from dispersion forces was comparable to, or greater than, that from the dipole-dipole interaction. This may result from difficulties in determining the damping zones for the various contributions to the cross sections.⁸ This difficulty is increased by the low resolution of our apparatus.

The relative collision diameters for nonpolar gases are given moderately well by the model of Bernstein and Rothe,^{12a} but are in poor agreement with those calculated from viscosity. However, the energy-transfer cross sections fit well to the viscosity-derived quantities for all gases except for the simplest ones (where collisional inefficiency causes much of the difference between energy transfer and viscosity values), and for aceto- and propionitriles.

The theories used to calculate collision properties are essentially liquid droplet theories in which the potentials add to create a central scattering element. Although the longer chain molecules in a *n*-alkyl homologous series are not spherical, their cross sections calculated on the basis of the droplet model are predicted to be the same as those of their branched analogs; disparities could arise since scattering elements distributed over an appreciable volume shield each other less than do centrally packed scattering centers.¹⁸ The latter expectation is borne out by energy-transfer data,¹⁹ but not by diffusion data¹⁸ nor probably by our scattering data.²⁰ The liquid droplet models predict a cross-sectional dependence on series number, *n*, of form $A + Bn^{2/3}$, for the larger molecules, where *A* and *B* are constants. The energy-transfer data reveal a stronger dependence on *n* than does the scattering. The explanation evidently lies with the range and nature of the interactions involved in the various kinds of experiment. Scattering depends on very weak interactions and the forces are long range compared to molecular dimensions. Energy transfer depends on stronger interactions and forces of range comparable to molecular dimensions. Thus, the results of the two types of experiment suggest that vibrational energy transfer in thermal unimolecular reactions depends primarily on strong, shorter range interactions which are nearly additive in the larger molecules, whereas scattering depends on long-range forces which increase as the approximate two-fifths power of the primary beam polarizability. However, the behavior of the lower nitriles in both types of experiment suggests that a coupling of dipoles plays a significant role in both phenomena.

(18) E. Fuller, K. Ensley, and C. Giddings, *J. Phys. Chem.*, **73**, 3679 (1969).

(19) L. Spicer and B. S. Rabinovitch, *ibid.*, **74**, 2445 (1970).

(20) An effect similar to this has recently been suggested as a possible source of larger-than-theoretical cross sections measured for the scattering of LiBr by Ar, Kr, and N₂ at very high resolution: see E. Richman and L. Wharton, *J. Chem. Phys.*, **53**, 945 (1970).