Historiography of a Very Fast Gas Reaction: A Case History That Spanned about 12 Decades

S. H. Bauer

Department of Chemistry and Chemical Biology, Cornell University, Ithaca, New York 14853

Contents

I. Introduction

Interconversions, whether physical or chemical, generally are not instantaneous but occur over a span of time. That must have been well appreciated by the alchemists. In the transmission of their received knowledge and secret formulas to their apprentices, they must have specified how long as well as how hot their experimental brews needed to be treated. Undoubtedly, they had theories as to why time was a practical parameter. However, there appears to be no record of attempts to quantitate the speed of a chemical conversion until about 1850 when Wilhelmy's pioneering study on the rates of inversion of cane sugar was published.[1] He defined a parameter (now designated a rate constant) and proposed an empirical expression for its temperature dependence. During the following three decades several empirical relations were suggested. van't Hoff in 1884 and Arrhenius in 1889 proposed the expression currently in general use.[2]

Measured reaction rates initially played a crucial role in identifying and classifying reaction mechanisms. Diagrams that purport to describe the sequence of changes in atom—atom connectivities induced by chemical conversions must have been proposed soon after chemists began to assign structures to molecules. The observed dependencies of rates of reaction on reactant concentration was then recognized as significant indicators of these dynamics. However, measurements of rates of reactions, their quantitative dependence on the concentrations of the participating species, and the temperature dependencies of the derived rate constants comprise but one significant component of the collection of data required for the development of a "mechanism". By now, the criteria for acceptable mechanisms have evolved and considerably tightened.

The designation "fast" for a chemical conversion implies a wide range of time scales, each characteristic of a reaction type. Fast associations, in contrast to fast dissociations, were investigated during the early decades of the 20th century. Clearly, such rates can be no faster than reactions between gaseous species that associate at every molecular encounter to generate adducts that have lifetimes greater than several picoseconds (so as to be detectable as a specific entity). Typical examples are recombinations of alkyl radicals,[3] reactions of Lewis acids with corresponding bases,[4] and the generation of alkali—metal halides when the metal vapors react with halogen gases.[5] To measure these very fast bimolecular associations, a variety of ingenious experimental techniques were developed.

The designation "fast" to an isomerization or a dissociation has undergone a "shrinking" process over the past decades, starting the 20th century with halftimes of milliseconds and ending with femtoseconds. The latter became possible via the evolution of laser technologies that provided intense localized radiation pulses and the means for controlling and measuring minute time intervals. These were supplemented by the development of analytical devices with highly enhanced sensitivities in species identification and detection.
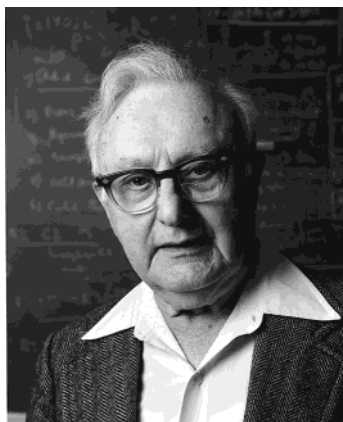
S. H. Bauer was born in Kaunas, Lithuania, on October 12, 1911. His family emigrated to the United States and settled in Chicago, IL. He became a U.S. citizen in 1927. He attended the University of Chicago and was granted the degrees Ph.B (1931) and Ph.D. (1935). There he studied with Profs. T. R. Hogness (his research director), W. D. Harkins, and H. I. Schlesinger. He then spent two years as a postdoctoral fellow at the California Institute of Technology, working with Profs. R. M. Badger and L. Pauling (infrared spectroscopy and electron diffraction). After serving as instructor in fuel technology at the Pennsylvania State University, he was invited to join the chemistry faculty at Cornell University (1939). He was promoted to professor in 1950. He retired from teaching in 1977 but continues with an active research program to the present. Bauer's publications deal with molecular structure determination by diffraction, EXAFS, and various spectroscopic techniques; measurements of some physical, thermochemical, and kinetic properties of the boranes; kinetics of fast reactions and spectral emissions at high temperatures as studied in shock waves and in chemical laser systems; mechanisms of pyrolysis of energetic materials (nitroalkanes); and models for condensation from supersaturated vapors. He is the author or co-author of 374 publications. Bauer was a Guggenheim Fellow (1949), an NSF Senior Postdoctoral Fellow (1962) at the CNRC and the Weizman Institute, and an NAS Interacademy Exchange Fellow, USSR (1966). In 1979 he receivd an Alexander von Humbold Award to spend 6 months at the Max Planck Institute of Quantum Optics in Garching-Munchen, Germany. In the fall of 1983 he was appointed the first foreign adjunct professor at the Institute of Molecular Science in Okazaki, Japan. He is a fellow of APS and AAAS and a memeber of Sigma Xi, Phi Beta Kappa, and ACS. He served as ACS lecture-tour speaker in 1975, 1976, 1977, 1980, and 1989. He was Sievers Lecturer, USC (1974); Emerson Lecturer, Emory University (1989), and Visiting Professor at North Dakota State University (1974), at University of California—Irvine (1978), and at University of California—Riverside (1978). Bauer served as consultant to the Los Alamos National Laboratory, the Argonne National Laboratory, ARCO at the Harvey Technical Center (1945–1985), and at Lockheed California (Skunk-works unit).

It is convenient to divide isomerization or bond dissociation reactions into two broad groups, one for stable species that require substantial activation to twist or fragment a designated bond, and a second of molecules that incorporate fluxional dynamics or a weak bond that is rapidly broken and reformed at ambient temperatures. For the former group the initiation event involves exposure to a source of external energy, such as photons, high-speed electrons, or high-temperature pulses (laser heating or shock compression). Then the time scale is determined by the intrinsic pulse rise time of the energy source and the response time (and sensitivity) of the analytical device. Currently, for complex conversions as well as for simple dissociations, it is possible to follow the separation of fragments on a femtosecond time scale.[6] For comparison, interatomic vibrational periods range from tens of femtoseconds, for tightly bound atom pairs, to picoseconds for fluxional oscillations.

This reveiw is restricted to the second group, dissociations [or isomerizations] wherein the parent species is in dynamic equilibrium with its products. Generally, such systems are described by conventional rate equations, expressed in terms of forward and reverse rate processes:

$$A \underset{k_f}{\overset{k_r}{\rightleftharpoons}} C; \quad A-B \underset{k_f}{\overset{k_r}{\rightleftharpoons}} A + B$$
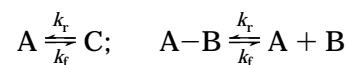
$$d[A]/dt = -k_f[A] + k_r[C];$$
$$d[A-B]/dt = -k_f[A-B] + k_r[A][B]$$

However, because both k_f and k_r are very large, initially every experimental sample is in an equilibrium, time-independent state. Then, any change in relative concentration must be preceded by a perturbation that temporarily displaces the sample as a whole from equilibrium. One measures the rate of return to equilibrium, that is, the "relaxation time" (τ), defined as the time span required for the system to return to $1/e$ of the displaced magnitude. Experimentally, perturbations have to be repeated for a range of initial concentrations, and from the measured relaxation times one may derive the conventional rate constants, based on an assumed mechanism. Examples of expressions for τ values in terms of k values, for a variety of mechanisms, are cited in most textbooks on chemical kinetics;[7] extended treatments are presented in several treatises.[8]

The rate of an isomerization is determined by the height of the "potential barrier". For an isomer pair of equal stability that interconvert via unimolecular kinetics, the relaxation time $\tau = 1/(2k)$, with $k \approx 10^{15} \exp(-E/RT)$. This is predicated under the limiting assumption that intramolecular rotational/vibrational relaxations are faster than the τ values for structural conversion or dissociation.[9] Therefore, one should not apply the above expression to τ values of $< \sim 10$ ps, for that is the time regime when internal relaxations (the redistribution of internal energy) and structural changes are coupled. Indeed, there are some "pathological" cases for which internal relaxations are incomplete for times as long as microseconds.[10]

Dissociation/association relaxation times follow a similar pattern. These τ values depend not only on the magnitude of the bond dissociation energies but also on the equilibrium concentrations of the bonded and dissociated species. Thus, for $AB \rightleftharpoons A + B$

$$\tau^{-1} = k_f + k_r([A]_e + [B]_e)$$

Again, intramolecular relaxations should be at least an order of magnitude shorter than the indicated τ for the above relation to be valid. Clearly, the rise time of the impulse step of the perturbation, in pressure, temperature, density, or irradiation, should be shorter than the chemical relaxation time. When the perturbation event is comparable in rise time to the latter, an "unfolding" computation is necessary for proper data reduction. Of course, the response times of the analytical devices must be within the same response period.

Formulations in terms of *relaxation times* were not generally utilized prior to about 1950.[11] An additional note of caution: whether rate constants derived from measured relaxation times (i.e., for conversions that take place when the systems are close to equilibrium) are identical with conventional rate constants, evaluated via measurements of changes in initial concentrations, when the parent species dominate, has been questioned.[12]
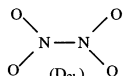
In the following we trace reports on the N_2O_4:NO_2 system that provide interesting illustrations of the evolution of diagnostic techniques for a simple, very rapid gas phase dissociation—how it was followed experimentally and theoretically for about 115 years.

II. N₂O₄:NO₂ Studies Prior to World War II

To date there are approximately 29 reports on measurements of the kinetics of the N_2O_4 dissociation (refer to Appendix 1). It is intriguing to inquire what particular features inspired such an extended scrutiny. In particular, it is instructive to note how increasingly sophisticated techniques have been exploited to fully describe the details of the dynamics of this equilibration. As noted above, this process was formulated in terms of forward and reverse rate constants and, thus, was tied to a specific mechanism. Prior to the discussion of these multifold kinetic studies, it is useful to list the currently accepted structural and thermochemical parameters for N_2O_4 and NO_2 (refer to Table 1).

In the initial insightful proposal by E. Nathanson and U. Nathanson dealing with this rapid equilibration,[13] the authors were concerned both with the partition between the two species at equilibrium, per the Guldberg—Waage principle of mass action, and the rates of attaining equilibrium. They considered how these depend on pressure and temperature [Table 2 is a summary of computed dimer/monomer ratios for a range of temperatures and total pressures [$p(t)$], based on the thermochemical parameters listed in Table 1]. The Nathansons noted that for a rapidly equilibrating mixture useful data could be derived from measurements of the heat capacities at constant pressure and at constant volume. In turn, the ratio of these quantities determines the speed of sound in the mixture. Prior to 1940, with the exception of the imaginative but ambiguous experiment by Brass and Tolman,[14] all 12 experimental and theoretical studies devoted to this kinetics problem focused on sound speed measurements. The underlying concept may be stated qualitatively. At any fixed location in a medium through which a sound wave is progressing, the material is subjected to periodic compressions and rarefactions. When the relaxation time for interconversion for a rapidly equilibrating pair of reactants is much longer than the alternating pressure pulses, the sound wave senses the system as a mixture of two distinct species. Thus, to very high frequency sound waves, the effective heat capacity of the mixture is the weighted sum of their individual heat capacities in proportion to their molar ratios. On the other hand, when the rates of interconversion are faster than the frequency of the alternating

Table 1. Structural and Thermochemical Parameters of NO₂ and N₂O₄[a]

	NO₂	N₂O₄
Molecular weight (gm/mol)	46.008	92.016
m.p. /b.p.	-11.2 / 21.2 C	
	yellow liq; brown gas	colorless
Structure (sym)	(C_v)	(D_{2h})
Interatomic distances(A)	N—O 1.202[b]	1.191[c]
	N—N	1.774
	<ONO 134.4	134.8°
Electronic ground state	$\tilde{X}\ ^2A_1$	$\tilde{X}\ ^1A_g$
Fundamental frequencies (cm⁻¹)	1665.5	1748;1710
	1357.8	1373;1261
	756.8	823;750;675
		480;430
		385;260;{50}
Thermochemistry (ideal gas)		
$\Delta H_f°$(298.15K): kcal/mol	7.93[d]	2.65[d]
S· (298.15K): eu	57.38	72.75
$\Delta H°$(dis): kcal/mol		13.21
$\Delta S°$(dis): eu		42.01
C_p(298K): cal/mol-K	8.89	8.93
$\Delta H_f°$(DFT calc at 298K[e]) : kcal/mol	8.08	{1.86}
Torsional barrier (G3Mp2B3[f]): kcal/mol		5.71
Near UV absorption:	diffuse: < 3972 A	colorless

The standard heat of vaporization of liq. N_2O_4 @ 298K is 6.84 kcal/mol. The quoted $\Delta H_f°$ of the liquid is -4.86 kcal/mol. The liquid boils at 294.2K; the gas phase consists of a mixture of dimers and monomers.

[a] Unless otherwise indicated, the listed values were abstracted from the JANAF Tables, updated Sept 30, 1964. [b] McClelland, B. W.; Gunderson, G.; Hedberg, K. *J. Chem. Phys.* **1972**, *56*, 4541. [c] Shen, Q.; Hedberg, K. *J. Phys. Chem. A* **1998**, *102*, 6470. [d] CRC Handbook of Chemistry and Physics, 82nd ed. [e] P. Politzer et al. *Recent Developments and Applications of Modern Density Functional Theory*; Elsevier Science: Amsterdam, The Netherlans, 1990; value in braces corrected for misprint. [f] Wilcox, C. F. *THEOCHEM* **2002**, in press.

Table 2. Equilibrium Ratios of N₂O₄/NO₂ for Various Temperatures and Pressures

T, K	K(eq), atm	p(tot)				
		1 atm	0.7 atm	0.5 atm	0.3 atm	0.1 atm
240	1.418E−3	26.02	21.79	18.33	14.10	7.90
260	1.194E−2	8.63	7.17	5.99	4.53	2.44
280	7.418E−2	3.21	2.61	2.14	1.55	0.764
300	3.612E−1	1.24	0.979	0.778	0.539	0.262
320	1.443	0.471	0.358	0.274	0.177	0.0651

compressions and rarefactions, the heats of association/dissociation are convoluted with the species heat capacities. Detailed analysis shows that the heat capacity ratio is consequently lowered by 3−5%. At some intermediate frequency, there is a transition in the magnitudes of the measured heat capacities. The ratio of effective heat capacities (γ) may be derived from measurements of sound speeds. Hence, at the intermediate frequency there occurs a corresponding change in measured speed of sound (designated dispersion). In the absence of precise values for the enthalpy of dissociation and of the heat capacities of the individual species, it is essential to identify the transition frequency to determine the chemical relaxation time.
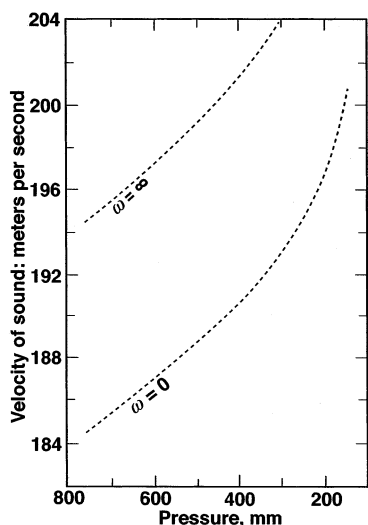
Figure 1. Velocities of sound calculated by Kistiakowsky and Richards, per Einstein's theoretical analysis, for N_2O_4:NO_2, as a function of sample pressure, at 25 °C. Illustrated are the two extreme cases for very low sound frequencies ($\omega = 0$) and very high frequencies ($\omega = \infty$).

The well-known Newton relation for sound speed reduces, for an ideal gas, to

$$a = [\gamma p/\rho]^{1/2} = [\gamma RT/M]^{1/2}; \qquad \gamma \equiv C_p/C_v$$

Note its similarity to the kinetic theory expression for the most probable molecular speed

$$u(mp) = [2RT/M]^{1/2}$$

Using Kundt tubes the Nathansons measured sound speeds in N_2O_4:NO_2 mixtures for a range of gas pressures. In 1914 Argo[15] reanalyzed their data and concluded that with the frequencies available to them they could not approach the dispersion region and, thus, could not detect any appreciable lag in equilibration rate during the alternating changes in pressure caused by the stationary sound waves.

That interconversion rates could be extracted from sound dispersion data is credited to Nernst, as reported in Keutel's doctoral dissertation.[16] Einstein's formulation[17] of the dependence of the velocity of sound on pressure, temperature, and the full range of sound frequencies for a reacting gaseous mixture had been accepted as the basic theoretical foundation for sound speed data reduction. It may be that it was in this connection that Einstein was reputed to have said, "Chemistry is too complicated to be left to the chemists". Figure 1 is a plot of calculated sound velocities in nitrogen tetraoxide at 25 °C, over a range of pressures, per Einstein's equations, for zero and for infinite frequencies. Later, Luck[18] showed that Einstein's analysis was incomplete, in that he assumed that the gases were ideal. Allowing for real gas behavior significantly reduced the magnitude of the difference between low- and high-frequency responses.

At the suggestion of Nernst, Selle[19] made a series of measurements of sound speeds for this system. In his paper he described the precautions he followed in preparing Kundt tubes for operation with the corrosive gases. By cementing metal pieces to the end walls, he was able to generate oscillations over a wide range of frequencies. He made many measurements at 21 °C and 500 mm pressure. He reported the following values: at $3630\ s^{-1}$, $a = 189.12$ m/s; at $3330\ s^{-1}$, $a = 188.70$ m/s; and at $1685\ s^{-1}$, $a = 186.12$ m/s. Thus, he claimed to have detected sound dispersion amounting to 2.2% of the measured sound speed. However, concurrently Gruneisen and Goens,[20] on the basis of their more extended measurements, with frequencies up to $15000\ s^{-1}$, covering the temperature range 10−35 °C and pressures og 265−760 mm, found that the velocity was independent of frequency to within a few tenths of a percent. Very brief reports by Olsen and Teeter[21] showed a slight increase in sound speed at $50000\ s^{-1}$, but those results were not confirmed.

In 1930 Kistiakowsky and Richards[22] introduced a major advance by utilizing a magnetostriction oscillator that had been invented by Pierce.[23] Thus, they were able to cover the frequency range of 9916−80350 cycles/s. Their measurements were made at 25.0 °C, at total sample pressures from 146 to 763 mm. For calibration of their equipment they recorded sound speeds for dry air (346.1−345.6 m/s), which were independent of pressure. For the tetraoxide mixtures they compiled their data with those of Gruneisen and Goens on a velocity versus pressure graph, per Einstein's equations, and found that the experimental curve crossed the $\omega = 0$ curve at 500 mm. For the pressure range 200−500 mm, the experimental points were marginally above $\omega = 0$, and at higher pressures, they were somewhat below $\omega = 0$, all within their estimated error margins. Thus, 80 kc proved to be below the dispersion frequency, and their measurements provided only a lower limit for the dissociation rate constant. For a rapidly equilibrating dissociation, such as

$$N_2O_4 \rightleftharpoons 2\ NO_2$$

the inflection frequency

$$\omega^* = \tau^{-1} = k_d[1 + p_{eq}(NO_2)/K_{eq}]$$

Hence, they could specify only that

$$k(d) \geq 4 \times 10^4\ s^{-1}$$

Kistiakowsky and Richards also demonstrated that the nitrogen oxide mixtures weakly absorbed sound waves, with magnitudes that increased when the impinging frequency approached the dispersion region. This is anticipated for all wave propagation, when there is a phase lag between the responding oscillations and the incident wave. Einstein derived expressions for the sigmoid shape of the dispersion region and of the corresponding bell-shaped absorption function.

On the western side of the continent, Brass and Tolman approached these elusive kinetics measurements using a novel and ingenious technique.[14] In their review of reports on sound velocity experiments, they called attention to an error of sign in Einstein's paper, not recognized by Kistiakowsky and Richards.
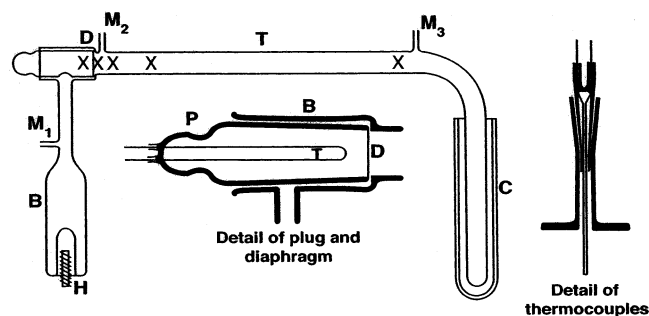
Figure 2. Composite of schematics of the apparatus used by Brass and Tolman. X's indicate the positions of the thermocouples.

[Thus, the calculated difference in velocities at 1 atm (25 °C) should be 3.8%, not 5.1% as shown in Figure 1.] The dimer/monomer gaseous mixture was forced through a perforated diaphragm that subjected the sample to a sudden drop in pressure (Figure 2), thus increasing the dissociation of the tetraoxide, which in turn led to a drop in temperature. From measured flow velocities and temperature differentials at various distances beyond the diaphragm, the dissociation rate constant for N_2O_4 was estimated. Indeed, they were fully aware of several troublesome features inherent in their experiments. Also, they called attention to an intrinsic ambiguity in formulating a mechanism for the dissociation. Their derived first-order rate constant ranged from 13.6 to 18.9 s^{-1} (mean = 15 s^{-1}), and they estimated a range of values for the bimolecular rate constant, at 1 atm and 25 °C, of $(4.2-8.2) \times 10^4$, not far from the lower limit set by Kistiakowsy and Richards. The concluding paragraph of their paper merits quoting: "The experiments which we have described are in any case of considerable interest, since they at least exhibit qualitatively a definite positive effect which can only be explained by a high rate of dissociation of nitrogen tetroxide, in contrast to the acoustic experiments which so far have led only to negative effects from which a high rate can be inferred".

That evaluation proved to be premature, for almost concurrently, Richards and Reid[24] reported on their acoustic experiments in an apparatus specifically designed for corrosive gases. They covered the temperature range of 0−30 °C and the pressure range 132−670 mm for frequencies from 9 to 451 kc, using a magnetostriction oscillator. They did reach the dispersion region. However, they were concerned with how to discriminate between relaxation effects due to dissociation and "heat capacity" contributions, because some nondissociating gases also show sound dispersion, due to lags in energy equilibration between translations/overall rotations and intramolecular vibrations, as first reported by Pierce.[23] For N_2O_4:NO_2, they considered a complex model and ultimately concluded that for these species lags in "heat capacities" need not be considered. Indeed, that is consistent with current theory. Rates of internal energy randomization are structure specific, but several generalizations have been recognized. Sufficiently rapid (on a picosecond time scale) energy redistributions take place intramolecularly via coupling between large-amplitude, low-frequency vibra-

tions and overall rotation and are induced during intermolecular collisions between species that carry dipoles and/or quadrupoles. With regard to the question of whether the dissociation was uni- or bimolecular, they noted that for any fixed temperature the derived rate constants did decrease (marginally) with decreasing pressure, as expected for a bimolecular process. Finally, Richards and Reid interpreted their data in terms of conventional kinetic rate theory. The quoted dissociation rate constant at 25 °C and 260 mm pressure is $k(d) = (4.8 \pm 0.5) \times 10^4$ s^{-1}, with an activation energy of 13.9 kcal/mol. (Contrast this with the currently accepted $\Delta H°$(dis) values, Table 1.)

About three months later Teeter[25] published a critical analysis of sonic dispersion experiments that were designed to determine the kinetic parameters for the nitrogen tetraoxide dissociation. He listed several unresolved problems, including the difficulty in discriminating contributions to dispersion due to lags in intramolecular energy redistribution versus dissociation and instrumental effects developed in small-diameter tubes. His measurements, with a large-diameter tube, did not show dispersion, but did indicate significant absorption, for frequencies up to 860 kc. He was particularly critical of Richards and Reid because in the analysis of their data they neglected the effects of absorption and assumed the gases were ideal. Also, there were errors in their mathematical derivations.

Teeter's critique elicited a lively response from Richards and Reid.[26] The latter considered in detail the potential for deriving useful data from absorption measurements. They concluded that due to intrinsic inaccuracies, they were unable to obtain a meaningful absorption coefficient at 450.1 kc and 260 mm pressure, in direct contradiction to Teeter's report. Dispersion, rather than absorption, provided the best route for evaluating the kinetic parameters. They reviewed the relevant mathematical relations, undertook an extensive error analysis of the data they recorded, and corrected a number of misprints that appeared in their first report. As a consequence of changing the magnitude of $\Delta H°$(dis) from 14.6 kcal/mol (in ref 24) to 14.0 kcal/mol, their derived reaction rate constant at 25 °C and 260 mm pressure rose to 5.3×10^4 s^{-1}, but their initially quoted activation energy (13.9 ± 0.9 kcal) was unchanged. For the following 20 years, these were the accepted values.

Uncertainties remained with respect to the relative contributions to dispersion due to lags in intramolecular energy redistribution versus rates of isomerization or dissociation. The earliest indication that some gases (CO_2 was the species of interest) showed dispersion (due to "heat capacity" lags) at high ultrasound frequencies was reported by Pierce,[23] who developed a quartz crystal controlled oscillator. More extended measurements were then made in his laboratory by Reid.[27] Interestingly, although the theory of ultrasound absorption by gases was developed in the middle of the 19th century, there were no reports on the relation between dispersion and absorption until the publication of a short paper by Herzfeld and Rice.[28]

III. Five Decades of Investigations, Post-World War II

During the early 1950s three gas dynamic techniques were extended to chemical kinetics investigations—use of shock tubes for imposing very rapid but controlled increases in temperature and pressure; fast flow past an "impact tube" that anchors a stationary shock in a flow field about a centrally held, small-diameter tube; and very rapid expansions through supersonic nozzles. It soon became evident that shock tubes were excellent retorts for gas kinetics investigations because they provided the means for operating over a wide range of temperatures and pressures. Indeed, these expectations have been amply fulfilled, as summarized in a series of reviews.[29] In contrast, impact tubes for measuring rapid relaxation times have limited applications and are somewhat difficult to control. This also applies to the manipulation of flows from supersonic nozzles.

An intrinsic difference between techniques should be noted: whereas ultrasound induces displacements from equilibrium that are minute, the perturbations from equilibrium resulting from shocks or supersonic expansions are substantial. One may question whether relaxation times measured under such widely different conditions are equivalent.[12] Tests specifically designed to answer this question, based on highly precise kinetic measurements, have yet to be made. It is conceivable that such a test could be provided by stochastic simulations of the two types of relaxation processes.

A shock wave is as step rise in pressure and temperature (rise times $\sim 0.1\ \mu s$) that propagates at supersonic speed (Mach number is defined as the ratio of shock velocity to sound speed in the medium ahead of the shock). The simplest configuration consists of a tube divided into two compartments by a thin diaphragm. One side is filled with a gas at high pressure (generally H_2 or He), designated "driver", and the other with a gas at low pressure (generally Ar admixed with $0.1-1.0\%$ of the reactant), designated "driven". When the diaphragm is punctured, a rapidly moving pressure pulse propagates down the low-pressure section. Sensors positioned along the tube wall record arrival times of the shock front and thus provide data for determining the shock speed. The magnitude of the pressure/temperature step is controlled by several experimental parameters. Temperature jumps that range from several tens of degrees to several thousand degrees can thus be generated.

The first use of a shock tube for measuring the dissociation rate of N_2O_4 was reported by Carrington and Davidson.[30] Because the dissociation enthalpy is low, very weak shocks were generated ($\Delta T \approx 25\ °C$; Mach 1.12) using N_2 at 2 atm for the driver and 1 atm N_2, admixed with 1% N_2O_4, in the driven section. It is generally accepted that the reactant species attains thermal equilibrium with the carrier gas within a few microseconds. The rate of production of NO_2 was followed photometrically via absorption of a light beam that passed normal to the axis of the tube. Data were obtained for shock temperatures that
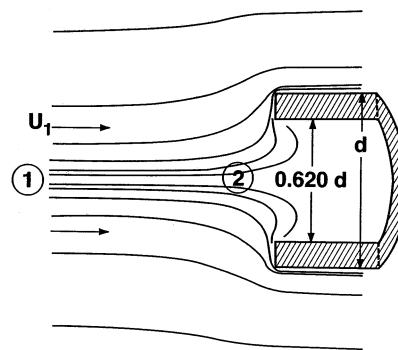

Figure 3. Streamlines for flow past an open-ended impact tube (for an incompressible fluid).

ranged from 252 to 310 K. To generate shocks at the lower temperatures, the tube had to be cooled. They evaluated rate constants for the bimolecular (second order) dissociation of the tetraoxide, with nitrogen molecules serving as collision partners. At 25 °C, $k(d) = 1.6 \times 10^6$ L/mol·s. From rate constants recorded over a 48 °C temperature interval they evaluated an activation energy of 11.0 ± 0.6 kcal/mol, compared with 13.9 ± 0.9 kcal/mol derived from sound dispersion measurements. Carrington and Davidson noted that at 25 °C, for 1% N_2O_4 in N_2, their interpolated dissociation rate constant was 8.3×10^4 s^{-1}, which compared well with the listed sound dispersion value of 6.6×10^4 s^{-1}. Finally, they suggested that because their derived activation energy for dissociation was lower than the measured dissociation enthalpy, the activation energy of the association rate constant for two NO_2 molecules must be negative, indicating that only relatively "cold" NO_2 molecules can stick together long enough to be stabilized by energy removal collisions with N_2. They estimated that the limiting first-order rate constant is $k(d)^{hpl} = 1 \times 10^{16} \exp(-12900/RT)$ s^{-1}.

The hydrodynamic description of the flow field developed in "impact tube" experiments, for measuring rapid relaxation times, is rather extended, and its description is best presented in Appendix 2 and Figure 3. Its application to N_2O_4:NO_2 kinetics was described by Bauer and Gustavson.[30,31] The average relaxation time thus derived for undiluted mixtures (at 25 °C) was approximately one-seventh that calculated for the bimolecular process on the basis of shock tube data. This may be explained as being due to the greater collision efficiency for excitation of the dissociating species by the same species compared to collisions with N_2.

Five years later Wegener[32] tested a rapid expansion configuration. He measured third-order recombination rate constants over the temperature range 215–290 K. Flows at Mach ≈ 2 were initiated through a supersonic nozzle from a reservoir at 400 K, filled with 0.01% mole fraction of NO_2 in N_2. The emerging gas was cooled at an estimated rate of $\approx 10^6$ K/s, to preselected low temperatures. In the downstream flow, the concentrations of NO_2 declined, relaxing to the equilibrium levels that corresponded to the temperatures of the downstream medium. The concentrations of NO_2 were measured photometrically, via a beam directed normal to the nozzle/flow axis. The rate of loss of NO_2 was evaluated from such
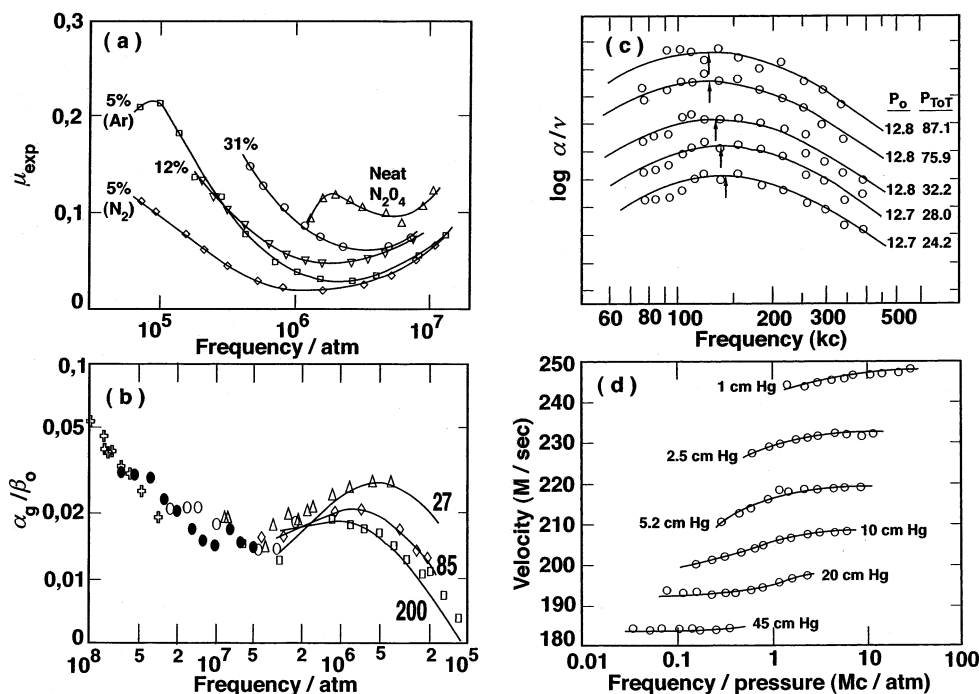
Figure 4. (a) Absorption coefficients, for 1 M Hz soundwaves, in neat and diluted mixtures of the oxides of nitrogen, at 20 °C:[34] in N_2; Ar; neat N_2O_4. Note the evolution of precision of measurements (a → d). (b) Absorption in N_2O_4:NO_2 mixtures at 20 °C for various total pressures:[35] ⊕, at 1 Torr; ●, at 3 Torr; ○, at 10 Torr; △, at 27 Torr; ◇, at 85 Torr; □, at 200 Torr. The full curves were computed. The horizontal scale is in cycles/atmosphere. (c) Dependence of absorption on total pressure; N_2O_4:NO_2 was diluted in N_2 at 15 °C.[36] P_o values are partial pressures of the oxides. (d) Dependence of sound speeds on frequency and pressure (at 20 °C).[37]

measurements for a range of Mach numbers. In his brief paper, the recombination rate constants showed much scatter, but his values did intersect those of Carrington−Davidson for the interval 250−270 K. Conceptually, Wegener's gas dynamic studies remind one of Tolman's 1932 experiments.

Toward the end of the decade the pendulum swung back to measurements with ultrasound for deriving relaxation times of rapidly equilibrating gaseous systems, with nitrogen tetraoxide as the representative species. The theory for dispersion and absorption of sound waves in real gases was revisited by Tabuchi.[33] He derived general expressions for sound wave transmission in rapidly reacting gases that obeyed the virial equation of state but showed no significant delays in attaining statistical equilibrium for intramolecular states. He stipulated that sound absorption due to viscosity, heat conduction, and radiation loss had to be separately corrected for.

Recall that an ideal, chemically stable gas does not absorb sound waves, nor does the speed of wave transmission depend on pressure. H. J. Bauer and co-workers[34] undertook the measurement of absorption in undiluted N_2O_4:NO_2 and in samples variously diluted with N_2 or Ar. They used an ultrasonic impulse unit that operated at a fixed frequency of 10^6 Hz and recorded absorption amplitudes (μ per unit wavelength) at 20 and 50 °C, for a wide range of total pressures (p). Their data, plotted in Figure 4a, show the variation of μ with $10^6/p$. At 20 °C, μ-(max) = 0.094; at 50 °C, μ(max) = 0.136. They emphasized that the derived relaxation times [estimated from the location of μ(max)] were determined by both the forward and reverse rate processes and proposed $\tau = 1.5 \times 10^{-6}$ s for the undiluted samples.

Their graphs clearly show that the relaxation times were dependent on the fractional composition of the mixtures with respect to the reacting species. In terms of conventional chemical kinetics formulations, the levels of dilution of the nitrogen oxides control the relative contributions of first-, second-, and third-order kinetic processes to the overall relaxation times.

A more extensive study was presented by Sessler.[35] He used electrostatic transducers based on solid dielectrics to cover an extended frequency range. Both sound velocities and absorptions were measured for pressures between 1 and 200 mmHg. The corresponding frequency/pressure ratios ranged from 10^5 to 10^8 (c/s)/atm. In the introduction to his paper Sessler reviewed in detail the publications that dealt with vibrational excitation of the dissociating species. Then, in an extended analysis he developed a mechanism in terms of a unimolecular dissociation that passes through an intermediate excited vibrational state. A summary of his experimental results, presented graphically, shows absorption coefficients versus ω/p for a range of pressures of neat samples, at 20 and 53 °C (Figure 4b). The dependence on pressure was clearly demonstrated; maxima appear in the range $10^6 > (\omega/p) > 5 \times 10^5$. The agreement between his computed and observed values is very good. Absorptions for the neat samples are considerably smaller than those reported by H. J. Bauer.[34] A second set of curves show sound speeds versus ω/p; the inflection points correspond to the maxima in absorption. Finally, he listed the previously published values for the dissociation rate constant of nitrogen tetraoxide, reduced to 20 °C and unit atmosphere,

for neat and diluted samples. They range from 0.53 $\times 10^5$ to 4.5×10^5 s^{-1}; Sessler's value is 1.7×10^5 s^{-1}.

A pulsed oscillator technique for measuring sound transmission in liquids (1956) was extended to gases in the early 1960s and to studies of N_2O_4:NO_2 equilibration rates. A pulsed oscillator was used to generate a burst of sound waves from a crystal or a microphone. Downstream the outputs from a receiving crystal (or microphone) and an amplitude-calibrated oscillator were recorded concurrently. The delays in amplitude of the burst in sound waves that traveled through the medium were thus measured. This development led to more precise data for both absorption and dispersion than was previously possible. Cher[36] recorded absorptions as a function of frequency for 78–394 kc/s in neat samples of the reactants and for mixtures diluted with N_2, Ar, and CO_2 (refer to Figure 4c). He observed that the maxima in absorption increased with increasing concentration of the tetraoxide, were nearly independent of the total pressure, and varied slightly with temperature, from 25 to 45 °C. He reduced these data by assuming a classical unimolecular mechanism, with limiting low- and high-pressure rate constants at 25 °C:

$$k(d)_{\text{lp}} = 4.5 \times 10^6 \text{ L/mol·s}$$

$$\text{and } k(d)_{\text{hp}} = 1.7 \times 10^5 \text{ s}^{-1}$$

Blend[37] used wide-band solid dielectric tranducers and measured sound velocities to an estimated reproducibility of 0.01%. He covered the frequency span from 1 kHz to 1 MHz, over a temperature range from −20 to +60 °C. (For typical data sets refer to Figure 4d.) He derived a relaxation time reduced to 1 atm at 30 °C: $\tau = 0.6$ μs.

In the intervening period Brokaw[38] considered the theory of thermal conductivity in reacting gases. He found that experimental values cited for N_2O_2:NO_2 were adequately described by his theory, on the basis of a bimolecular rate constant, at 296 K of $k(d)_{\text{lp}} =$ 5.3×10^6 L/mol·s. Mathematical models for heat transfer in gas-cooled nuclear reactors, taking into account the kinetics of chemical reactions, were also developed by Tverkovkin et al.[39]

The use of shock waves to impose a step rise in temperature was tested again in 1970. Zimet,[40] working in Wegener's laboratory, utilized the technique of "fully dispersed" waves, that is, very weak waves with shock speeds between the equilibrium and frozen sound speeds, to measure the dissociation rate of N_2O_4. Clearly, shock waves generated in conventionally structured shock tubes induce temperature jumps that are too large to be useful for following the kinetic changes in rapidly equilibrating systems with very low energies of activation. Zimet fitted his data to a bimolecular dissociation mechanism, assuming that the activation energy was ≈11 kcal/mol, proposed by Carrington and Davidson.[30] His cited pre-exponential factors are 2.2×10^{14} for Ar as a collision partner and 2.9×10^{14} for N_2.

The development of readily manipulated laser units that emit significant intensities of selected monochromatic radiation provided a novel means for rapidly perturbing chemical systems. Controlled temperature jumps could be produced by absorbed radiation pulses when (a) the laser frequency is absorbed by one of the reactants; (b) the available frequency is absorbed by an admixed chemically inert species that rapidly transfers its excitation (vib → trans; rot) to all of the molecular species present in the volume illuminated by the laser beam; and (c) direct photolysis of one of the reactants (generally in the UV). In 1984 Gozel et al.[41] used a TEA laser to irradiate mixtures of N_2O_4:NO_2, Ar, and low levels of SiF_4 (which has a strong absorption in the IR, at 1031.5 cm^{-1}). Thus, via method b, he induced temperature jumps of ≈5−10 °C. The consequent rate of production of additional NO_2 was followed photometrically by recording its absorption at 400 nm. His measured relaxation times were reduced to association rate constants for a bimolecular process. A typical set of his operating conditions is as follows: 8 bar Ar + 4.9 mbar N_2O_4:NO_2 + 370 μbar SiF_4 at −20 °C. He measured relaxation times for a range of pressures of the diluents (Ar, N_2, or He) and attempted to follow the kinetics of association in the "falloff" pressure range. The following values were cited for 0.8 bar Ar, for the temperature interval −32 to +14 °C:

$$k(a) =$$
$$2.2 \times 10^{11} \exp(+2.2 \text{ kcal/mol}/RT) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$$

$$k(d) = 3.8 \times 10^{11} \exp(-10.8 \text{ kcal/mol}/RT) \text{ s}^{-1}$$

The positive exponential energy for association is not inconsistent with the value proposed by Carrington and Davidson. However, the corresponding magnitude Gozel derived when N_2 was the diluent appears to be unacceptable.

An extended set of experiments was undertaken by Borrell and co-workers[42] to measure, at 298 K, the pressure dependence of the association rate constant. They covered the pressure range 1−207 bar and thus determined the shape of the "falloff" curve. They used method c, that is, 20 ns pulses of a KrF laser, operating at 248.4 nm, to dissociate N_2O_4, and followed the return to its equilibrium level by recording absorption of the photolized gas at 220 nm. The diluent gas was N_2. Although the nascent NO_2 molecules are generated in excited electronic states (A or B), these are rapidly quenched (within nanoseconds). At high N_2 pressures no significant rise in sample temperature was thus induced. However, at ∼1 bar the released energy generated a small increment in temperature, estimated to be of the order of 0.8 K. Corrections were introduced for the dependence of absorption coefficients on pressure, to the equilibrium constant for the rise in temperature, and for several additional minor factors.

Borrell used Troe's statistical adiabatic channel model[48] to calculate resolved energy and angular momentum state specific rate constants. It appears that these have pronounced maxima at very low energies. Their final data are plotted in Figure 5, including a superposed value published by Zimet[40] and four values cited by Carrington and Davidson.[30] The large pressure range used in these measure-
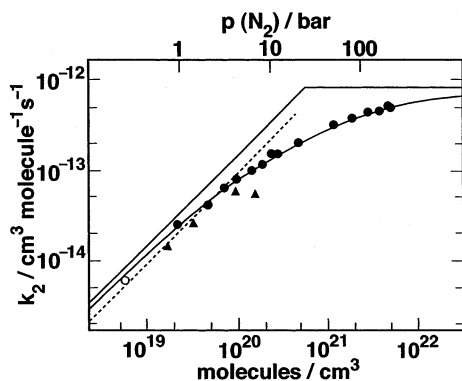
Figure 5. Falloff curve for NO_2 association rate constants (diluted in N_2) at 300 K. The solid curve connects data points measured by Borrell et al. (Appendix 1, entry 26). The point ○ is the single value reported by Zimet (Appendix 1, entry 23); ▲ represent values derived from the first shock tube experiments by Carrington and Davidson (Appendix 1, entry 14).

Figure 6. Typical resonance curve recorded for the first radial mode of the cylinder used by Fiedler and Hess (Appendix 1, entry 28). Note their partition of contributions from several sources to the overall response curve.

ments, at 298 K, permitted deriving both the low- and high-pressure limiting values for the association rate constants:

$$k(a)^{hpl} = 8.3 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

$$k(a)^{lpl} = 1.4 \times 10^{-3} ([N_2]) \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1}$$

Using Troe's analysis they derived temperature-dependent values for the range $300 < T/K < 600$:

$$k(a)^{hpl} = 8.3 \times 10^{-13} (300/T)^{1.1}$$

$$k(d)^{hpl} = 7.7 \times 10^{-15} (300/T)^{1.1} \exp (-6460/T) \text{ s}^{-1}$$

The relaxation time of N_2O_4:NO_2 subjected to a mild perturbation was also measured by the optoacoustic technique. That radiation pulses in absorbing media generate corresponding sound waves has been known for more than 120 years. A. G. Bell's empirical tests were described in 1880,[44] and concurrently, there appeared reports of laboratory experiments by Röntgen[45] and Tyndall.[46] Then 48 years elapsed before Russian investigators used optoacoustics for chemical analysis. Currently, there are 515 citations listed on the World Wide Web that describe optoacoustic devices for measuring a variety of material properties.

The sound waves generated via pulsed radiation lag in phase relative to those of exciting radiation. This appears to have been first noted by Slobodskaya,[47] who related the phase-lag to the vibrational relaxation time in CO_2. Later, Turrell measured the vibrational lifetime of excited CO.[48] Vibrational relaxation times in CO_2 were remeasured for wet and dry samples for both low and high pressures by Jacox.[49] Since then highly improved techniques for generating controlled light pulses, along with increased sensitivity and precision in detecting sound waves, have led to a virtual explosion of applications of optoacoustic devices.

For measurements of the relaxation time of nitroxide gases following a thermal perturbation, two variants of the optoacoustic effect were utilized, designated "resonant" and "nonresonant" detection
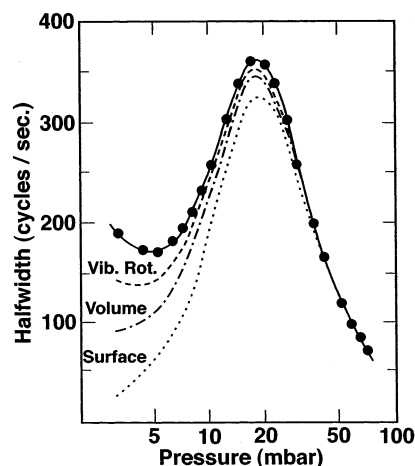
of the sonic signals. These refer to the response of the cell to the minute pressure modulations. In a preliminary investigation Roozendael and Herman[50a] demonstrated that the populations of rotational levels of NO_2 and N_2O_4 were perturbed by incident pulses of Ar laser radiation (at 488 nm) and that as a consequence rapid but minute jumps in temperature were induced. They described[50b] a nonresonant optoacoustic probing of the heat dissipation rate in N_2O_4:NO_2 mixtures. Of special note is their introduction of a high-sensitivity condenser-type microphone in their cylindrical acoustic cell. Again, any relaxation process that is slower than the chopping frequency shifts the phase and amplitude of the acoustic signal. Both were measured under a variety conditions for chopping frequencies of 40–320 Hz, in neat samples at 2.2, 3.8, 5.5, and 6.5 Torr. They defined a pressure-independent relaxation time, $\tau° = \tau/p$, and derived $\tau° = 5 \times 10^{-5}$ s/Torr at 25 °C. For the corresponding second-order dissociation rate constant, $k°(d)/p$, they proposed $k°(d) = 1.5 \times 10^2$ s^{-1}/Torr, which reduces to $k(d) = 2.6 \times 10^6$ L/mol·s.

A more extended set of measurements was described by Fiedler and Hess[51] using a resonant acoustic cell. Standing waves were excited by an amplitude-modulated Ar laser, and the sound waves were detected with an electred microphone inserted in the side of a thermally stabilized stainless steel cylinder. Carefully designed optical and electronic components characterize these measurements. They tested neat samples over a range of low pressures, at various temperatures (273–317 K). A detailed theoretical model for such resonators was developed for correlating sound frequency dispersion, absorption, and resonance broadening of the acoustic signals. Figure 6 illustrates the partition of their detector response curve to contributions from several relaxation sources. In a table they compared seven published values for reciprocal relaxation times $(1/\tau)$ for neat samples, at 298 K, reduced to 760 Torr, which were derived from sound dispersion or absorption measurements. These range from 1.5×10^5 to 2.3×10^5 s^{-1}. Fiedler and Hess favor the lower value. The corresponding bimolecular dissociation rate con-

stants (reduced to 298 K) range from $k(d) = 8.9 \times 10^{-15}$ to 4.3×10^{-15} cm^3 molecule^{-1} s^{-1}. Fielder and Hess favor 6.1×10^{-15}, an intermediate value. Thus, there is general agreement for magnitudes of kinetics parameters evaluated from acoustic relaxation time measurements, but there is one perturbing value. The activation energy for N_2O_4 dissociation proposed by Fielder and Hess is 8.6 kcal/mol, which is ~3 kcal lower than that derived via other techniques.

At this stage perhaps one may regard measurements of N_2O_4:NO_2 relaxations via acoustic devices primarily as means to validate the technique rather than for providing firmer values for the relaxation times that characterize that rapidly equilibrating system. It appears that nitrogen tetraoxide is a "strange" compound, not only with respect to its kinetics of dissociation but also with respect to its electronic structure. DFT calculations[52] of thermochemical and structural parameters for the five analogous X_2N-NX_2 species (X = O, CN, F, CH$_3$, and H) present sharp contrasts between N_2O_4 and the other four. The N–N bond length in the tetraoxide is 1.78 Å compared to 1.44–1.48 Å in the species with X = CN, F, CH$_3$, and H. However, the barrier for rotation out of the planar configuration (D_{2h}) was measured to be 1900 cm^{-1}.[53] The <ONO angle is 134°, very close to that in the monomer. The corresponding <XNX angle is 123° in the tetracyano species and between 102° and 108° in the others.

During the past two decades, newly developed laser pulse techniques, for studies of optical properties in the femtosecond time range, modified some of the questions previously addressed in molecular mechanics and thus had an influence on classical models used in chemical kinetics. Molecular motions during some dissociation events can now be followed in detail in that time regime.[6] Not surprisingly, the ground electronic state dynamics of N_2O_4 was studied by Dantus and co-workers[54] using nonresonant femtosecond time-resolved four-wave mixing (<15 fs pulses at 90 MHz, centered at 805 nm). The irradiated mixtures were tested over a range of temperatures—from 294 K (80% N_2O_4) to 363 K (94% NO_2), at various pressures. Fast vibrational dynamics were recorded for N_2O_4 and assigned to v_3 of the N–N bond stretching oscillation. Some NO_2 photoproducts were found following N_2O_4 excitation.

The direct photodissociation of N_2O_4 at 193 nm yields one NO_2 in its ground electronic state and an electronically excited NO_2, in either $^4B_2$ or $^2B_2$.[55] Thus, the dissociation process via energetic photons is not comparable to thermal dissociation. The possibility of using femtosecond electron diffraction recording[56] of structural changes that the NO_2 fragments undergo during N–N bond fission via UV photolysis is intriguing, but that information will only complement the 115 year quest for the ultimate description of the thermal dissociation event.

IV. Acknowledgements

V. Appendix 1: Timeline of Reports on N_2O_4 = $2NO_2$ Kinetics

(1) Nathanson, L.; Nathanson, E. *Ann. Phys.* **1885**, *24*, 454; **1886**, *26*, 606.
(2) Brass, P. D.; Tolman, R. C. *J. Am. Chem. Soc.* **1932**, *54*, 1003.
(3) Keutel, F. *Doc. Diss. Berlin* **1910**.
(4) Argo, W. L. *J. Phys. Chem.* **1914**, *18*, 438.
(5) Einstein, A. *Berliner Berichte* **1920**, *18*, 381.
(6) Gruneisen, E.; Goens, E. *Ann. Phys* **1923**, *72*, 193.
(7) Selle, H. *Zeit. Phys. Chem.* **1923**, *104*, 1.
(8) Olsen, A. R.; Teeter, C. E. *Nature* **1929**, *124*, 444; **1930**, *125*, 150.
(9) Kistiakowsky, G. B.; Richards, W. T. *J. Am. Chem. Soc.* **1930**, *52*, 4661.
(10) Luck, D. G. C. *Phys. Rev.* **1932**, *40*, 440.
(11) Richards, W. T.; Reid, J. A. *J. Chem. Phys.* **1933**, *1*, 114.
(12) Teeter, C. E. *J. Chem. Phys.* **1933**, *1*, 251.
(13) Richards, W. T.; Reid, J. A. *J. Chem. Phys.* **1933**, *1*, 737.
(14) Carrington, T.; Davidson, N. *J. Phys. Chem.* **1953**, *57*, 418.
(15) Bauer, S. H.; Gustavson, M. R. *Discuss. Faraday Soc.* **1954**, *17*, 69.
(16) Tabuchi, D. *J. Chem. Phys.* **1955**, *23*, 2033.
(17) Wegener, P. P. *J. Chem. Phys.* **1958**, *28*, 724.
(18) Bauer, H. J.; Kneser, H. O.; Sittig, E. *Acustica* **1959**, *9*, 181.
(19) Sessler, G. *Acustica* **1960**, *10*, 44.
(20) Brokaw, R. *J. Phys. Chem.* **1961**, *35*, 1569.
(21) Cher, M. *J. Chem. Phys.* **1962**, *37*, 2564.
(22) Blend, H. *J. Acoust. Soc. Am.* **1970**, *47*, 757.
(23) Zimet, E. *J. Chem. Phys.* **1970**, *53*, 515.
(24) Abstract of a report presented at a conference in Novosibirsk in **1983** (translation not available): "The dispersion of sound velocity in N_2O_4–Ar mixtures was studied over the whole concentration range at 0.26–5.2 MHz, 0.995–0.2 MPa, and 314–423 K. The results are discussed with respect to the application of the acoustic method to the study of kinetics of dissociation of N_2O_4."
(25) Gozel, P.; Calpini, B.; van de Bergh, H. *Isr. J. Chem.* **1984**, *24*, 210.
(26) Borell, P.; Cobos, C. J.; Luther, K. *J. Phys. Chem.* **1988**, *92*, 4377.
(27) van Roozendael, M.; Herman, M. *Chem. Phys. Lett.* **1989**, *166*, 233.
(28) Fiedler, M.; Hess, P. *J. Chem. Phys.* **1990**, *93*, 8693.
(29) Pastrick, I.; Comstock, M.; Dantus, M. *Chem. Phys. Lett.* **2001**, *349*, 71.

VI. Appendix 2: Impact Tube Experiments

The impact tube configuration was devised by A. K. Kantrowitz to measure the vibrational relaxation time of CO_2 (*J. Chem. Phys.* **1946**, *14*, 150). From a

reservoir, the gas at equilibrium (at p_0, T_0, α_0 is the degree of dissociation) is allowed to expand adiabatically and isentropically through a properly shaped nozzle. For this slow expansion equilibrium is maintained so that the gas at the exit of the orifice, now at a lower pressure, temperature, and degree of dissociation (p_1, T_1, and α_1), comprises the "prepared" sample. The enthalpy of the gas in a coordinate system moving with it, at its mass velocity (u_1) is less than that in the reservoir by $Mu_1^2/2$ per mole. Downstream uniform streamline flow continues until the gas approaches within about one diameter from the face of the impact tube (Figure 3). That obstruction introduces a stagnation region in the vicinity of the central streamline. The velocity of the gas flowing along this streamline is thus reduced to zero. An enthalpy equal to $Mu_1^2/2$ is thereby injected into the gas during the time that it takes to traverse a distance about half the diameter of the tube. Were all of the molecular degrees of freedom to equilibrate with the rate of enthalpy input, the pressure and temperature of the gas after this adiabatic and isentropic compression would be equal to that in the initial reservoir. However, when the relaxation time for the molecular degrees of freedom is slower than the rate of injection of enthalpy, the gas at stage 2 does not attain thermodynamic equilibrium. Then, the transition from stage 1 to stage 2 is adiabatic but not isentropic. As the gas reverts to equilibrium at the mouth of the impact tube into which the relatively stationary gas is diffusing it gains entropy, which is measured by the pressure difference ($p_0 - p_2$) for a range of p_0/p_1 ratios, which determine u_1. ($p_0 - p_2$) is a measure of the desired relaxation rate, integrated over time.

VII. References

(1) Wilhelmy, L. *Pogg. Ann.* **1850**, *81*, 413.
(2) van't Hoff, J. H. *Études de Dynamique Chemique* **1884**. Arrhenius, S. *Zeit. Phys. Chem.* **1889**, *4*, 226.
(3) Trotman-Dickenson, A. F. *Gas Kinetics*; Academic Press: New York, 1955.
(4) Smith, F. T.; Klistiakowsky, G. B. *J. Chem. Phys.* **1959**, *31*, 621.
(5) Polanyi, M. *Atomic Reactions*; Ernest Benn: London, U.K., 1932.
(6) Zewail, A. H. *J. Phys. Chem.* **2000**, *104*, 5660.
(7) Laidler, K. J. *Chemical Kinetics*, 3rd ed.; Harper and Row: New York, 1987.
(8) Bernasconi, C. F. *Relaxation Kinetics*; Academic Press: New York, 1976.
(9) Bauer, S. H. *Chem. Rev.* **1978**, *78*, 147.
(10) Kiefer, J. H.; Buzyna, L. L.; Dib, A.; Sundaram, S. *J. Chem. Phys.* **2000**, *113*, 48. Borchard, B.; Bauer, S. H. *J. Chem. Phys.* **1986**, *85*, 4980.
(11) Eigen, M. *Discuss. Faraday Soc.* **1954**, *17*, 194.
(12) Widom, B. *Science* **1965**, *148*, 1555.
(13) Nathanson, L.; Nathanson, E. *Ann. Phys.* **1885**, *24*, 454; **1886**, *26*, 606.
(14) Brass, P. D.; Tolman, R. C. *J. Am. Chem. Soc.* **1932**, *54*, 1003.
(15) Argo, W. L. *J. Phys. Chem.* **1914**, *18*, 438.
(16) Keutel, F. *Doc. Diss. Berlin* **1910**.
(17) Einstein, A. *Berliner Berichte* **1920**, *18*, 381.
(18) Luck, D. G. C. *Phys. Rev.* **1932**, *40*, 440.
(19) Selle, H. *Zeit. Phys. Chem.* **1923**, *104*, 1.
(20) Gruneisen, E.; Goens, E. *Ann. Phys.* **1923**, *72*, 193.
(21) Olsen, A. R.; Teeter, C. E. *Nature* **1929**, *124*, 444; **1930**, *125*, 150.
(22) Kistiakowsky, G. B.; Richards, W. T. *J. Am. Chem. Soc.* **1930**, *52*, 4661.
(23) Pierce, G. W. *Proc. Am. Acad. Sci.* **1925**, *60*, 269; Pierce, G. W. *Proc. Am. Acad. Sci.* **1928**, *63*, 1.
(24) Richards, W. T.; Reid, J. A. *J. Chem. Phys.* **1933**, *1*, 114.
(25) Teeter, C. E. *J. Chem. Phys.* **1933**, *1*, 251.
(26) Richards, W. T.; Reid, J. A. *J. Chem. Phys.* **1933**, *1*, 737.
(27) Reid, C. D. *Phys. Rev.* **1930**, *35*, 814.
(28) Herzfeld, K. F.; Rice, F. O. *Phys. Rev.* **1928**, *31*, 691.
(29) Bauer, S. H. *Annu Rev. Phys. Chem.* **1965**, *16*, 245. Belford, R. L.; Strehlow, R. A. *Annu. Rev. Phys. Chem.* **1969**, *20*, 247. Tsang, W.; Lifshitz, A. *Annu. Rev. Phys. Chem.* **1990**, *41*, 559. Michael, J. V.; Lim, K. P. *Annu. Rev. Phys. Chem.* **1993**, *44*, 429.
(30) Carrington, T.; Davidson, N. *J. Phys. Chem.* **1953**, *57*, 418.
(31) Bauer, S. H.; Gustavson, M. R. *Discuss. Faraday Soc.* **1954**, *17*, 69.
(32) Wegener, P. P. *J. Chem. Phys.* **1958**, *28*, 724.
(33) Tabuchi, D. *J. Chem. Phys.* **1955**, *23*, 2033.
(34) Bauer, H. J.; Kneser, H. O.; Sittig, E. *Acustica* **1959**, *9*, 181.
(35) Sessler, G. *Acustica* **1960**, *10*, 44.
(36) Cher, M. *J. Chem. Phys.* **1962**, *37*, 2564.
(37) Blend, H. *J. Acoust. Soc. Am.* **1970**, *47*, 757.
(38) Brokaw, R. *J. Chem. Phys.* **1961**, *35*, 1569.
(39) Tverkovkin, B. E. (complete reference not available); published in: *Nauka 1 Tekhnika*; Beloruss, 1970.
(40) Zimet, E. *J. Chem. Phys.* **1970**, *53*, 515.
(41) Gozel, P.; Calpini, B.; van de Bergh, H. *Isr. J. Chem.* **1984**, *24*, 210.
(42) Borell, P.; Cobos, C. J.; Luther, K. *J. Phys. Chem.* **1988**, *92*, 4377.
(43) Troe, J. *J. Chem. Phys.* **1983**, *76*, 6017.
(44) Bell, A. G. *Proc. Am. Assoc. Adv. Sci.* **1880**, *29*, 115.
(45) Röntgen, W. C. *Ann. Phys. Chem. Ser. 3* **1881**, *12*, 155.
(46) Tyndall, J. *Proc. R. Soc. London* **1881**, *31*, 307.
(47) Slobodskaya, P. V. *Isvet. Akad. Nauk Fiz* **1948**, *12*, 656.
(48) Turrell, G. C. Ph.D. Dissertation, Oregon State University, 1954.
(49) Jacox, M. E.; Bauer, S. H. *J. Phys. Chem.* **1957**, *61*, 833.
(50) (a) van Roozendael, M.; Herman, M. *Chem. Phys. Lett.* **1989**, *166*, 233. (b) van Roosendael, M.; Herman, M. *Chem. Phys.* **1989**, *139*, 391.
(51) Fiedler, M.; Hess, P. *J. Chem. Phys.* **1990**, *93*, 8693.
(52) Wilcox, C. F.; Bauer, S. H. *THEOCHEM* **2002**, in press.
(53) Koput, J.; Seibert, J. W. G.; Winnewisser, B. P. *Chem. Phys. Lett.* **1993**, *204*, 183.
(54) Pastrick, I.; Comstock, M.; Dantus, M. *Chem. Phys. Lett.* **2001**, *349*, 71.
(55) Mueller, J. A.; Morton, M. L.; Curry, S. L.; Abbatt, J. P. D.; Butler, L. J. *J. Phys. Chem. A* **2000**, *104*, 4825.
(56) Lobastov, V. A.; Srinivasan, R.; Goodson, B. M.; Ruan, C.-Y.; Feenstra, J. S.; Zewail, A. H. *Science* **2001**, *291*, 458.