

found in the present particles is in accordance with the expected contribution from the surface due to the larger surface to volume ratio. With a magnetic anisotropy of this size the first term of eq 1 is approximately equal to the second term at $B = 0.55$ T, and therefore it cannot be neglected.

In order to estimate the error in the particle size determination, introduced by neglecting the magnetic anisotropy energy, we have computer-simulated spectra of superparamagnetic α -Fe with various values of K and in different applied magnetic fields.¹⁰ These investigations show that in the present case the error in the particle size determination by use of eq 3 is less than 5%.

It is interesting to note that the isomer shift and quadrupole splitting of the 2.5-nm α -Fe particles are within experimental error equal to those of bulk α -Fe. Also B_0 , the saturation hyperfine field, is, after correction for the influence of the demagnetizing field, equal to that of bulk α -Fe, within experimental error. Thus,

(10) Clausen, B. S.; Christensen, P. H.; Mørup, S., to be published.

in spite of the extremely small particle size, the particles behave, apart from the superparamagnetic relaxation phenomena, essentially as bulk α -Fe.

The present Fe/C-1 catalyst provides a very interesting sample for fundamental studies of superparamagnetic relaxation in metallic iron. As α -Fe particles with a diameter of 2.5 nm contain less than 700 atoms, of which about one third are at the surface, the Fe/C-1 catalyst offers also possibilities to investigate the influence of adsorbed gases on the magnetic behavior of the metal atoms at the surface. Measurements of the Fe/C-1 sample at temperatures below that of liquid nitrogen and in magnetic fields up to 7 T are now in progress.

Acknowledgment. The authors acknowledge support from the Netherlands Organization for the Advancement of Pure Research (Z.W.O.) and the Danish Council for Scientific and Industrial Research.

Registry No. Iron, 7439-89-6; carbon, 7440-44-0.

Electronic Excitations in Bicyclohexylidene

Michael Allan,

Institute for Physical Chemistry, University of Fribourg, Switzerland

P. A. Snyder,

Department of Chemistry, Florida Atlantic University, Boca Raton, Florida 33431

and M. B. Robin*

AT&T Bell Laboratories, Murray Hill, New Jersey 07974 (Received: July 23, 1985)

A reinvestigation of the electronic excited states of the olefin bicyclohexylidene has been carried out using the techniques of photoelectron, electron impact, and multiphoton ionization spectroscopies. Our studies show that the multitude of sharp structures in the vapor spectrum (40 000–65 000 cm^{-1}) are due to Rydberg excitations originating at the π MO of the olefin chromophore. These excitations are near degenerate as a consequence of the extreme alkylation of the olefin and are separable only by combining photoelectron and threshold electron impact techniques. The anomalously high intensities of the overlapping Rydberg bands are due to two underlying valence excitations, whereas only one ($\pi \rightarrow \pi^*$) is expected. Two transitions also appear in the crystal spectrum in the same energy region and correlate with the underlying valence excitations of the vapor phase rather than with the more prominent Rydberg promotions; it is suggested that the second valence transition is due to a $\pi(\text{CH}_2) \rightarrow \pi^*$ intramolecular charge transfer involving the cyclohexyl rings and the double bond. The two-photon selection rules evident in the multiphoton ionization spectrum of bicyclohexylidene point to C_{2h} symmetry in the vapor phase.

Introduction

In general, the parade of electronic excitations in the alkyl olefins below 8 eV is quite regular, with the pattern of $\pi \rightarrow 3s$, $\pi \rightarrow 3p$, and $\pi \rightarrow 3d$ Rydberg excitations interrupted only by the intrusion of the $\pi \rightarrow \pi^*$ valence excitation in the vicinity of the transition to $3s$.¹ Valence transitions between π and σ valence MO's occur at yet higher energies and rarely have been identified with any confidence.

The various Rydberg excitations in alkyl olefins have been identified as such on the basis of (a) the term values of the excitations (ionization potential minus the excitation energy), (b) the spectral response to external perturbation on going from the vapor phase to a condensed phase, and (c) their oscillator strengths, *f*. Elaborating on the above points, the term values of Rydberg transitions terminating at $3s$, $3p$, and $3d$ Rydberg orbitals fall in the ranges 27 000–21 000, 21 000–18 000, and 14 000–11 000 cm^{-1} , respectively, with the variation within each range related directly

to the number and bulk of the pendant alkyl groups. Note that in the limit of very large alkyl groups (10 or more carbon atoms per molecule), the term values of transitions terminating at $3s$ and $3p$ in olefins are nearly equal.

When studied in absorption, the Rydberg bands of a molecule's vapor-phase spectrum are so strongly perturbed on going into solution or into a solid phase² that they often are cited as "missing" in the condensed-phase spectra. Studies of this effect using the circular dichroism of chiral derivatives show that the Rydberg bands upon external perturbation are not "missing" but are broadened and shifted to higher frequencies.^{1,3,4} Lowering the temperature of such solutions further shifts the CD band centers to higher frequencies. In contrast, a valence excitation such as $\pi \rightarrow \pi^*$ will be shifted to lower frequency upon entering the condensed phase, and lowering the temperature has no further effect on the transition frequency. As for the oscillator strength distinction between Rydberg and valence transitions in the alkyl

(1) M. B. Robin, "Higher Excited States of Polyatomic Molecules", Vol. III, Academic Press, New York, 1985.

(2) A. Gedanken, B. Raz, and J. Jortner, *J. Chem. Phys.*, **58**, 1178 (1973).

(3) A. F. Drake and S. F. Mason, *Tetrahedron*, **33**, 937 (1977).

(4) K. P. Gross and O. Schnepf, *Chem. Phys. Lett.*, **36**, 531 (1975).

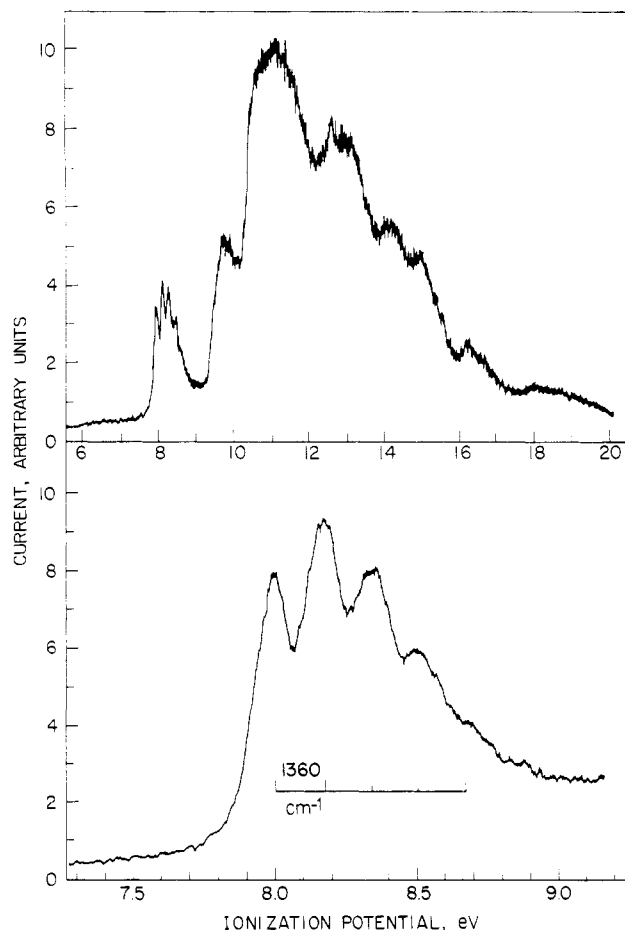
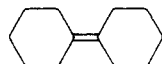


Figure 1. He I photoelectron spectrum of bicyclohexylidene in the vapor phase (upper panel), and detail of the first band (lower panel).

olefins, it is sufficient to note that, whereas the oscillator strength of a nondegenerate Rydberg excitation always is less than 0.08, that for the $\pi \rightarrow \pi^*$ valence excitation is in the 0.2–0.3 range.

Among alkyl-olefin spectra, that of bicyclohexylidene (BCH)



is exceptional, for it seems not to follow the olefin spectral pattern discussed above. The absorption spectrum of BCH vapor shows two intense features, $f = 0.19$ and 0.26 , centered at $48\,000$ and $55\,000\text{ cm}^{-1}$.⁵ Though the sharp vibronic structures in these bands are much more suggestive of Rydberg excitations than of $\pi \rightarrow \pi^*$ valence bands, their oscillator strengths are much more compatible with valence transitions, and furthermore, there is otherwise no discrete feature in the absorption spectrum which can be assigned as $\pi \rightarrow \pi^*$. Moreover, the reflection spectrum of a single crystal of BCH shows distinct transitions centered at $48\,000$ and $51\,000\text{ cm}^{-1}$, each of which has perfect long-axis polarization. By virtue of their appearance in the solid phase, it is clear that the two bands of the crystal are valence excitations. Snyder and Clark⁵ tentatively assigned these crystal transitions of BCH as $\sigma \rightarrow \sigma^*$ and $\pi \rightarrow \pi^*$, respectively, and correlated them with the two transitions at $48\,000$ and $55\,000\text{ cm}^{-1}$ in the vapor spectrum. Needless to say, the assignment of a $\sigma \rightarrow \sigma^*$ transition as the lowest in an alkyl olefin is unexpected. However, the important point is that there are two low-lying valence transitions in the crystal spectrum, both polarized along the double bond.

The sum total of these observations on the BCH spectrum leads to a picture which in almost every detail is at variance with that normally accepted for olefin absorption. As we now have more spectroscopic data on BCH in the vapor phase, we feel that a more detailed interpretation can be given for the vapor spectrum, though

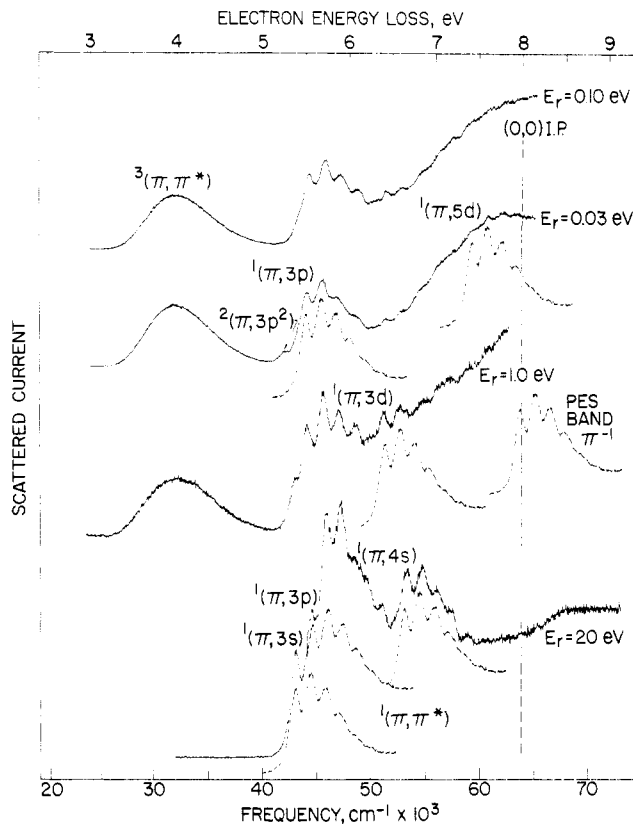


Figure 2. Electron energy loss spectra of bicyclohexylidene at constant residual energy E_r . The dashed curves are the $(\pi)^{-1}$ photoelectron band envelopes (Figure 1, bottom), positioned so as to coincide with the Rydberg excitations originating at the π MO.

a convincing interpretation of the crystal spectrum remains a problem. The new data on BCH encompass photoelectron, multiphoton ionization, solution absorption, and electron-energy-loss spectra.

Photoelectron Spectrum

The photoelectron spectrum (PES) of BCH (Figure 1) is most useful in interpreting its excitation spectrum on two counts. First, it allows one to compute term values with respect to the π orbital ionization potential, and, second, the Franck–Condon envelope of the $(\pi)^{-1}$ PES band is expected to resemble closely the corresponding envelopes of the $\pi \rightarrow nR$ Rydberg bands in the optical spectra. The vibronically structured band at 8.137 eV ($65\,630\text{ cm}^{-1}$) in the PES of BCH (Figure 1) is the $(\pi)^{-1}$ ionization; the 1360-cm^{-1} progression evident in this band presumably corresponds to C=C stretching in the ionic state. The electron energy loss spectrum of BCH (vide infra) shows ground-state vibrational bands at 2880 cm^{-1} (C–H stretch) and 1350 cm^{-1} (C=C stretch). Since there are 12 ionizations in the 10–17-eV region of cyclohexane,⁶ it is safe to assume that there are many more PES bands in the 9–18-eV region of BCH than the 8 or so that are resolved in Figure 1. We note that the energy of the $(\pi)^{-1}$ PES band of BCH is in no way unusual for a heavily alkylated olefin.

Energy-Loss Spectra

Energy-loss spectra of BCH were determined with a trochoidal electron impact spectrometer operated at constant residual energy, E_r .⁷ Spectra determined in this way having E_r of 20 eV or larger are known to approximate closely the electric-dipole spectrum as recorded optically, whereas with E_r equal to 1 eV or less, the optical selection rules can be strongly violated. In this case, both spin-forbidden and orbitally forbidden excitations may appear with

(5) P. A. Snyder and L. B. Clark, *J. Chem. Phys.*, **52**, 998 (1970).

(6) K. Kimura, S. Katsumata, Y. Achiba, T. Yamazaki, and S. Iwata, "Handbook of He I Photoelectron Spectra of Fundamental Organic Molecules", Japan Scientific Societies Press, Tokyo, 1981.

(7) M. Allan, *Helv. Chim. Acta*, **65**, 2008 (1982).

TABLE I: Term Values and Rydberg Assignments in the Spectrum of Bicyclohexylidene

(0,0) energy, eV	term value, ^a cm ⁻¹	upper state assignment
5.396	20 750	(π , 3s)
5.49	20 000	(π , 3p)
5.574	19 300	(π , 3p')
6.41	12 570	(π , 3d)
6.67	10 500	(π , 4s)
7.41 (?)	4 500	(π , 5d) (?)
7.969	0	IP

^a Measured with respect to the (0,0) band of the PES spectrum at 7.969 eV.

high relative intensities, and temporary-negative-ion (TNI) states also may form, giving rise to valence and Feshbach resonances. All of these effects are seen in BCH.

It is clear from the variation of the energy-loss spectra of BCH run at different residual energies, Figure 2, that the spectra consist of several structured but overlapping bands, with relative intensities that depend strongly upon E_r . We have analyzed the energy-loss spectra by first scaling the (π)⁻¹ Franck-Condon band of the PES to fit the energy-loss scale and then seeking coincidences between this Franck-Condon envelope and those in the spectra, being mindful both of vibronic intervals and of relative Franck-Condon factors. The six bands found in this way are assigned as Rydberg excitations originating at the π MO, as shown in Figure 2 and in Table I.

Orbital assignments of the Rydberg bands of BCH are made on the basis of the term-value criteria stated above. As expected, the highly structured part of the spectrum proves to involve Rydberg excitations, in this case with $\pi \rightarrow 3s$ and $\pi \rightarrow 3p$ almost degenerate as appropriate for a molecule at the alkyl limit. Distinct transitions to 3p and 3p' result from the fact that the (π)⁻¹ cationic core has low symmetry. Transitions to 3d are well removed from those to 3s and 3p, as expected, but close to $n = 4$ members of transitions to ns and np .

The Rydberg nature of the structured bands of BCH is confirmed by their response to external perturbation. Dissolution of BCH in pentane yields a spectrum in the 40 000–59 000-cm⁻¹ region consisting of broad peaks at 48 500 and 56 000 cm⁻¹; the sharp vibronic structure of the vapor phase is no longer present in the solution spectrum.

Three other features are seen in the electron-impact spectra. A band in the electron transmission spectrum at 2.25 eV (18 100 cm⁻¹) corresponds to the valence TNI resonance in which the incident electron is momentarily captured in the π^* MO; this electron-affinity value is in accord with π^* resonances observed in other alkyl olefins [1.78 to 2.27 eV (14 400 to 18 300 cm⁻¹) in ethylene and the methylethylenes].⁸ A broad energy-loss band centered at 3.97 eV (32 000 cm⁻¹) in BCH is appropriate for assignment to the ³(π, π^*) state in an alkyl olefin [4.32 to 4.10 eV (34 800 to 33 100 cm⁻¹) in ethylene and the methylethylenes].⁹ Since both of these excitations involving the π^* MO have energies within the normal range observed for alkyl olefins, and since the (π)⁻¹ ionization potential is similarly normal, one must conclude that there is nothing unusual about the π -electron system in BCH.

A resonance observed at 5.25 eV (42 300 cm⁻¹) in the near-threshold energy loss spectrum with $E_r = 0.03$ eV is identified as a Feshbach negative-ion state by the fact that it shifts down in energy loss with increasing residual energy. The corresponding Feshbach configuration would appear to be ²($\pi, 3p^2$) on the basis of a 2000-cm⁻¹ decrement with respect to the ¹($\pi, 3p'$) configuration.¹

Multiphoton Ionization Spectra

The MPI spectrum of BCH is relevant to the question of assignments in the optical and energy-loss spectra, for the MPI

TABLE II: Comparison of MPI and Optical Spectra of BCH

MPI one-photon wavelength, Å	MPI two-photon resonance, eV	optical absorption peaks, eV
		5.391
4488	5.525	5.577
4347	5.700	5.712
4210	5.89	5.882
4055	6.115	{ 6.051
		{ 6.199
3870	6.41	6.354
		6.525

spectra reveal Rydberg resonance states but not valence resonance states.^{1,10} Moreover, if the symmetry of the molecule is high, then the appearance and/or nonappearance of transitions in the one-photon and two-photon spectra relate directly to the symmetries of the excited states. The MPI spectrum of BCH vapor in the one-photon wavelength range 5000–3580 Å (20 000–27 900 cm⁻¹) reveals resonance peaks as recorded in Table II; beyond a two-photon energy of 6.5 eV (52 400 cm⁻¹), the MPI spectrum is intense but structureless. Comparison of the MPI peak energies as two-photon resonances with the one-photon absorption peaks, Table II, shows several apparent coincidences. However, the excitation to 3s with a one-photon origin at 5.391 eV (43 480 cm⁻¹) is *not* seen in the MPI spectrum even though it is energetically feasible as a (2 + 1) transition.

Discussion

It is clear from the above analysis that the structured bands of BCH vapor in the 43 000–60 000-cm⁻¹ region are Rydberg excitations originating at the π MO. The term values observed for these bands are typical of those seen for chromophores at the alkyl limit. Because such Rydberg excitations do not persist in condensed phases, the structured bands of the 43 000–60 000-cm⁻¹ region of the vapor are *not* related to those of the crystal spectrum in the 43 000–55 000-cm⁻¹ region.

The absence of the $\pi \rightarrow 3s$ transition and the presence of the $\pi \rightarrow 3p$ band in the MPI spectrum at the two-photon level follows the selection rules appropriate to ethylene itself,¹¹ suggesting that BCH in the vapor phase has C_{2h} symmetry as in the crystal.¹² Because $\pi \rightarrow 3p$ is forbidden in the one-photon spectrum of the C_{2h} molecule, it is postulated that the appearance of this band in the optical spectrum is induced by odd quanta of C=C torsion. The low-frequency allowing mode is expressed as the difference of optical and MPI origin frequencies but our resolution does not allow an accurate measurement of this. In support of this scenario, we note that the variation of energy loss in the $\pi \rightarrow 3p$ region with E_r is strongly suggestive of dipole-forbidden excitations.

This interpretation of the new spectral data on BCH leads to a picture which parallels that for other alkyl olefins up to a point. There is nothing outwardly unusual about the π/π^* manifold in this molecule in the vapor phase, but the Rydberg structure is complicated by the fact that the $\pi \rightarrow 3p$ manifold is split into three poorly resolved transitions which in turn are nearly degenerate with $\pi \rightarrow 3s$. Once shorn of its Rydberg bands, the spectrum of BCH in pentane solution shows *two* low-lying valence bands, which presumably are responsible for the high molar extinction coefficients observed for the 48 000- and 55 000-cm⁻¹ peaks of the vapor-phase spectrum. These peaks seemingly correlate with those of the crystal in the same spectra region; however, the apparent vibronic structures of the crystal transitions are strangely missing from the vapor and solution spectra. The clear presence of two intense valence excitations in the region of the lowest Rydberg bands is perplexing, for only one is expected. The earlier assignments of the second feature as either $\pi(\text{CH}_2) \rightarrow \pi^*$ or $\pi \rightarrow \sigma^*$ or $\sigma \rightarrow \sigma^*$ have yet to be tested.^{5,13,14} It appears that the

(10) P. M. Johnson, *Acc. Chem. Res.*, **13**, 20 (1980).

(11) A. Gedanken, N. A. Kuebler, and M. B. Robin, *J. Chem. Phys.*, **76**, 46 (1982).

(12) K. Sasvári and M. Löw, *Acta Crystallogr.*, **19**, 840 (1965).

(13) M. B. Robin, "Higher Excited States of Polyatomic Molecules", Vol. II, Academic Press, New York, 1975.

(8) K. D. Jordan and P. D. Burrow, *J. Am. Chem. Soc.*, **102**, 6882 (1980).

(9) W. M. Flicker, O. A. Mosher, and A. Kuppermann, *Chem. Phys. Lett.*, **36**, 56 (1975).

spectra of alkyl olefins are more complicated than previously acknowledged, though the complications may be evident only in certain highly alkylated systems.

One tempting clue as to the identity of the second valence excitation in BCH comes from the photoelectron work of Heilbronner et al. on the "ribbon orbitals" of species containing the cyclohexane ring.¹⁵ The orbitals in question are related to the highest-filled MO's of cyclohexane ($4e_g$) and are composed of $\pi(\text{CH}_2)$ and $\sigma(\text{CC})$ local orbitals.⁶ According to the photoelectron study, the ribbon MO's are separated from the tangle of the other π , σ MO's by an appreciable gap in compounds containing the

cyclohexyl group. The ribbon MO's of BCH are observed at 9.8 eV in the photoelectron spectrum of Figure 1. As a result of their low ionization potential, the ribbon orbitals "are good donor orbitals and ... they must play an important, if not dominant role in intramolecular charge transfer processes".¹⁵ Extension of this idea leads directly to the assignment of the two low-lying valence transitions of BCH as $\pi \rightarrow \pi^*$ and $\pi(\text{CH}_2) \rightarrow \pi^*$, the latter being largely an intramolecular charge-transfer transition from the cyclohexyl group to the double bond. Both of these transitions are allowed with long-axis polarization.

Acknowledgment. Financial support of the Swiss National Science Foundation (Project No. 2.219-0.84) and the United States National Science Foundation (Grant CHE-8416312) are gratefully acknowledged, as are several discussions of these spectra with Dr. Aharon Gedanken.

Shock-Tube Study of the Rate Constant for Excited $\text{OH}^*(^2\Sigma^+)$ Formation in the $\text{N}_2\text{O}-\text{H}_2$ Reaction

Yoshiaki Hidaka,* Hirokazu Takuma,[†] and Masao Suga[†]

Advanced Instrumentation Center for Chemical Analysis, and Department of Chemistry, Ehime University, Bunkyo-cho, Matsuyama 790, Japan

The $\text{OH}^*(^2\Sigma^+)^2\Pi$ chemiluminescence in $\text{N}_2\text{O}-\text{H}_2$ highly diluted with Ar was studied over the temperature range 1400–2000 K behind reflected shock waves. From the relationship between OH^* concentration and temperature in three mixtures it was determined that OH^* was mainly formed by $\text{H} + \text{O} + \text{M} = \text{OH}^* + \text{M}$ (1) and $\text{N}_2\text{O} + \text{H} = \text{N}_2 + \text{OH}^*$ (6). The rate constant of reaction 6 was found to be $(1.6 \pm 1) \times 10^{14} \exp(-50300/RT) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$.

Introduction

The mechanism and rate constant expressions for electronically excited $\text{OH}^*(^2\Sigma^+)$ formation in the high-temperature oxidation of H_2 by O_2 have been studied in detail.¹⁻⁶ It was found to be formed mainly by the reaction $\text{H} + \text{O} + \text{M} = \text{OH}^* + \text{M}$ with $k = 1.2 \times 10^{13} \exp(-6940/RT) \text{ cm}^6 \text{ mol}^{-2} \text{ s}^{-1}$.⁶ The OH^* emission in the high-temperature oxidation of H_2 by N_2O has been studied only by Soloukhin,⁷ who inferred $\text{H} + \text{N}_2\text{O} = \text{OH}^* + \text{N}_2$ as the reaction forming OH^* and discussed the relationship between OH^* and OH.

A detailed study of the rate constant of OH^* formation in the high-temperature oxidation of H_2 by N_2O has not yet been reported. This work, therefore, was carried out to clarify the identity and the rate constant of the reaction forming OH^* in the high-temperature oxidation of H_2 by N_2O .

Experimental Section

The apparatus and procedures used in this study are essentially the same as described previously.⁶ Emission was monitored with a Hamamatsu R-306 photomultiplier after passing through an interference filter ($\lambda_{\text{max}} = 3055 \text{ \AA}$, half-width = 150 \AA) located behind a quartz window of the shock tube and through two slits either 0.18 and 0.24 mm wide separated by a cylindrical tube 2 cm long. Infrared emission through two 0.8-mm slits and an interference filter ($\lambda_{\text{max}} = 4.68 \text{ }\mu\text{m}$, half-width = $0.1 \text{ }\mu\text{m}$) was observed with Fujitsu IV-200C4 InSb detector to learn the time variation of N_2O concentration. The ultraviolet and infrared emissions were observed simultaneously behind reflected shock waves. The OH^* concentration was determined from the OH^* emission intensity by using the relationship between OH^* concentration and voltage found before.⁶ Data interpretation was carried out by computer simulations essentially as described previously.⁶

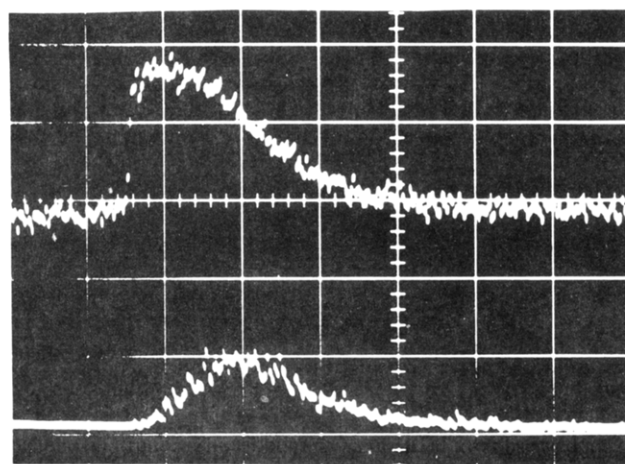


Figure 1. Typical oscillograms of N_2O IR thermal emission (upper trace) and OH^* UV chemiluminescence emission (lower trace). The sweep speed is $100 \text{ }\mu\text{s}/\text{division}$; mixture B, $T_5 = 1612 \text{ K}$, $P_5 = 2.14 \text{ atm}$.

Three reaction mixtures were employed: (A) 2.0% N_2O , 1.0% H_2 , 97.0% Ar; (B) 1.0% N_2O , 1.0% H_2 , 98.0% Ar; (C) 1.0% N_2O , 0.5% H_2 , 98.5% Ar. The H_2 and Ar, specified to be 99.9% and 99.99% pure, respectively, were obtained from commercial cylinders and used without further purification. The commercial-

(1) W. C. Gardiner, Jr., K. Morinaga, D. L. Ripley, and T. Takeyama, *Phys. Fluids Suppl.*, **1**, 120 (1969).

(2) D. Gutman, R. W. Lutz, N. F. Jacobs, E. A. Hardwidge, and G. L. Schott, *J. Chem. Phys.*, **48**, 5689 (1968).

(3) S. Ticktin, G. Spindler, and H. I. Schiff, *Discuss. Faraday Soc.*, **44**, 218 (1967).

(4) T. Koike and K. Morinaga, *Bull. Chem. Soc. Jpn.*, **49**, 1457 (1976).

(5) T. Koike and K. Morinaga, *Bull. Chem. Soc. Jpn.*, **55**, 52 (1982).

(6) Y. Hidaka, S. Takahashi, H. Kawano, M. Suga, and W. C. Gardiner, Jr., *J. Phys. Chem.*, **86**, 1429 (1982).

(7) R. L. Soloukhin, *Symp. (Int.) Combust., [Proc.]*, **14th**, 77 (1973).

* Advanced Instrumentation Center for Chemical Analysis.

[†] Department of Chemistry.