tion does not apply to the breadth of the methyl and para proton lines. The ring line is slightly asymmetric because the para proton line is not completely broadened and experiences a different contact shift from the ortho and meta proton lines.

The radical ions are undoubtedly associated with counterions. Eastman and collaborators[3] have shown that in the sodium salt of tetracyanethylene dissolved in benzene containing a crown ether the ion association is complete. Although our ESR spectra do not exhibit unambiguous symptoms of ion pairing, the slowness of the electron transfer process—some four orders of magnitude less than the encounter controlled limit observed in other solvents—is undoubtedly related to the ion pairing.

Since submission of this communication we have seen the recent article by Kaempf et al.,[4] which reports ESR observations identical with ours. The article reports neither NMR observations nor estimates of electron transfer rates.

Acknowledgment. This work has been supported by the National Science Foundation and by the donors of the Petroleum Research Fund, administered by the American Chemical Society, to whom grateful acknowledgment is made.

References and Notes

(1) M. P. Eastman, G. V. Bruno, and J. H. Freed, *J. Chem. Phys.*, **52**, 2511 (1970).
(2) M. P. Eastman, R. G. Kooser, M. R. Das, and J. H. Freed, *J. Chem. Phys.*, **51**, 2690 (1969).
(3) M. T. Watts, M. L. Lu, R. C. Chen, and M. P. Eastman, *J. Phys. Chem.*, **77**, 2959 (1973).
(4) B. Kaempf, S. Raynal, A. Collet, F. Schue, S. Boileau, and J. Lehn, *Angew. Chem., Int. Ed. Engl.*, **13**, 611 (1974).

M. A. Komarynsky, S. I. Weissman*
Department of Chemistry, Washington University
St. Louis, Missouri 63130
Received November 21, 1974

Stimulated Raman Scattering from H_2 Gas for Fast Heating in Laser-Temperature-Jump Chemical Relaxation Experiments

Sir:

We report the use of the stimulated Raman effect in hydrogen gas at 60-80 atm[1,13,15,16,17,18] in the construction of a versatile laser-temperature-jump spectrophotometer for very fast kinetic measurements with the chemical relaxation technique.[2] By the Raman effect in hydrogen gas, the original wavelength of 1.06 μ, obtained from a Q-switched Nd^{3+}-glass giant-pulse laser, is shifted to 1.89 μ. The infrared absorption of H_2O and of other compounds at this wavelength has already been studied extensively in aqueous,[3] nonaqueous,[4] organic, and mixed solvents[5] and in electrolyte[6] and nonelectrolyte[7] solutions.

The H_2 Raman-laser system has a definite advantage over the use of liquid N_2 (with a Raman shift to 1.41 μ) as reported by Sutin et al.,[8,12] because the H_2 Raman cell can be permanently installed outside the laser cavity and needs not to be refilled.

In our experiment a 2 J/20 nsec pulse from a Nd^{3+}-glass laser at 1.06 μ (beam diameter about 12 mm), which is Q-switched by a Pockels cell, is focused by a fused quartz lens (Spectrosil) of 50-cm focal length into a 1 m long pressure cell filled with H_2 at 80 atm. The distance between the lens and the pressure cell is about 10 cm. The light beam emerging from the pressure cell is collected by a second infrasil lens and is directed after filtering into a thin absorption cell containing the sample, which it abruptly heats. The conversion of 1.06 to 1.89 μ is normally about 20% or more.[9] The conversion efficiency from 1.06 to 1.89 μ radiation after filtering off 1.06 μ with a BG18 filter was measured by a "Control Data Corporation's" Ballastic Thermopile Model 100 attached to Keithley Instrument Inc. Microvolt Ammeter Model 150 B.

Water has a big absorption band at 1.9 μ.[10] The converted energy produces vibrational heating of the solvent, which induces temperature-jump chemical relaxation effects of solute molecules. The 1.06 μ radiation is completely filtered off by a Schott's green glass BG18 filter placed between the pressure cell and the collecting lens. The BG18 filter has no transmittance between 1 and 1.2 μ but transmits about 62% radiation at 1.89 μ which is used for temperature-jump effects.

For aqueous solutions a double spacer absorption cell with three 2 mm thick infrasil windows is used. The front spacer thickness is 0.5 mm; the back spacer is 5 mm. The absorbing sample solution is in the front layer. The back layer contains pure water and is used as a filter, removing any remaining ir energy, and serves at the same time for thermostating purposes. A monochromatic observation beam traverses the spacer cell in about the same direction as the heating beam.

The H_2 Raman shifted pulse width is sharpened when compared with the original 1.06 μ unconverted pulse;[11] thus very rapid heating rise times can be produced, using the stimulated Raman effect of H_2 gas for temperature-jump spectrophotometry or for other fast reaction kinetic measurements. The observed half-width of the converted pulse (using an EG & G's SGD-100 type photodiode) was 12 nsec. The pulse width reduction of 1.06 to 1.89 μ in H_2 gas is a known phenomenon expected due to the nonlinear relation between exciting and stimulated wave field amplitudes. The power level in the converted pulse is correspondingly enhanced.

We have investigated the effect of using a second high pressure cell following the one previously described, which increases the net effective total focal volume for SRS, with the intention of obtaining a larger energy output from an additional conversion of the remaining 1.06 μ radiation. In this case more than 40% total conversion efficiency as measured by CDC Model 100 Ballastic Thermopile has been obtained, indicating that the second conversion is influenced by the modes of the 1.89 μ radiation already present in the beam. In these experiments the second pressure cell was only 500 mm long; the beam emerging from the first cell was refocused in this second cell by a set of infrasil lenses of 50 cm focal length, 10 cm apart; the distance of the focal point to the exit window of the second pressure cell was about 10 cm. As was already observed before,[9] the stability of the converted pulse energy is improved. This is important for obtaining reproducible amplitudes of the temperature change in T-jump experiments.

The extinction coefficient of H_2O at 1.89 μ is 128 cm^{-1}. There may be some advantage in frequency doubling the 1.89 μ radiation by suitable crystals, which would also make available the weaker absorption bands of H_2O at 0.97 μ.

For studies of the kinetics of association-reactions, this laser-temperature-jump-spectrophotometer is very suitable.

Acknowledgment. We are grateful to Professor Fritz P. Schäfer of our institute and Professor J. Ducuing of the University of Paris, Orsay, for many consultations and we are indebted to Dr. A. Müller and G. Willenbring of our institution and to Dr. Z. Schelly of the University of Georgia, and Dr. G. Ilgenfritz of the University of Köln, Germany,

for help and discussions. S.A. is obliged to Professor M. Eigen for encouragement.

References and Notes

(1) J. Ducuing, G. Jeffrin, and J. P. Coffinet, *Opt. Commun.*, **2** (6) (1970); also J. Ducuing et al., *Phys. Rev. Lett.*, **17**, 117 (1966).
(2) M. Eigen and L. De Maeyer, "Techniques of Organic Chemistry", Vol. VIII, Part 11, A. Weissberger, Ed., Interscience, New York, N.Y., 1963.
(3) R. Goldstein and S. S. Penner, *J. Quant. Spectrosc. Radiat. Transfer*, **4**, 441-451 (1964).
(4) K. B. Whetsel, *Appl. Spectrosc. Rev.*, **2**, 1-67 (1968).
(5) G. R. Choppin and M. R. Violante, *J. Chem. Phys.*, **56** (1972).
(6) Landolt-Börnstein, "Zahlen, Werte und Funktionen aus Physik, Chemie, Astronomie, Geophysik, Technik", Bd. 6, Teil 2, p 469, 1951.
(7) G. H. Czerlinski, "Chemical Relaxation", Marcel Dekker, New York, N.Y., 1966.
(8) N. Sutin, J. V. Beitz, G. W. Flynn, and D. H. Turner, *J. Am. Chem. Soc.*, **94**, 1554 (1972); **92**, 4130 (1970).
(9) J. Ducuing, Institut d'Optique, University of Paris, Orsay, Paris, France (private communications).
(10) W. A. Luck, *Ber. Bunsenges. Phys. Chem.*, **69** (1965).
(11) N. G. Basov, A. N. Oraevskii, and A. F. Suchkov, *Hetf. Pis. Red.*, **16**, 301-304 (1972).
(12) J. B. Grun, A. K. McQuillan, and B. P. Stoicheff, *Phys. Rev.*, **180** (1969).
(13) P. Lallemand and P. Simova, *J. Mol. Spectrosc.*, **26**, 262-276 (1968).
(14) H. L. Welsh, M. F. Crawford, and J. C. F. McDonald, *Phys. Rev.*, **83**, 1264 (1951).
(15) W. Schmidt and W. Appt, "Carl Zeiss, Forschungsgruppe", 7082 Oberkochen, West Germany.
(16) R. W. Minck, R. W. Terhune, and W. G. Rado, *Appl. Phys. Lett.*, **3**, 181 (1963).
(17) N. Bloembergen, G. Bret, P. Lallemand, P. Pine, and P. Simova, *IEEE J. Quantum Electron.*, **3**, 197 (1967).
(18) J. A. Durado, F. M. Johnson, and L. J. Nugent, *IEEE J. Quantum Electron.*, **4** (1968).
(19) This work is based on the Ph.D. dissertation of S.A.

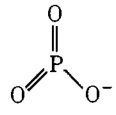
Syed Ameen,*[19] Leo De Maeyer
Max-Planck-Institut für biophysikalische Chemie
Göttingen, West Germany

Received August 27, 1974

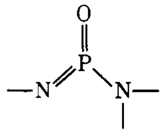
The Three-Phase Test for Reaction Intermediates. Metaphosphates

Sir:

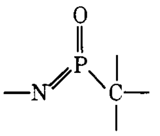
Monomeric metaphosphates have been implicated as intermediates in a variety of phosphorus transfer reactions.[1,2] The hydrolysis of monoalkyl,[3] aryl,[4] and acyl[5] phosphates and the decomposition of β-halophosphonates[6] can all be interpreted as proceeding via the elusive parent ion, I. Kinetic evidence has similarly indicated II, a metaphosphorimidic amide, during the hydrolysis of phosphorodiamidic halides and pyrophosphates,[7] whereas stereochemical evidence has been used to support the intermediacy of III, a metaphosphoniminate.[8] Most recently, trapping[9] and spectroscopic[10] evidence for metaphosphate intermediates have been presented and prompt this report of new evidence for the intermediacy of II, using an experimental technique which differs *in kind* from previous methods.



I



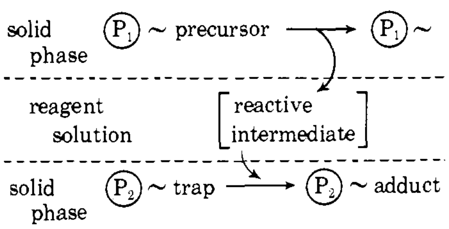
II



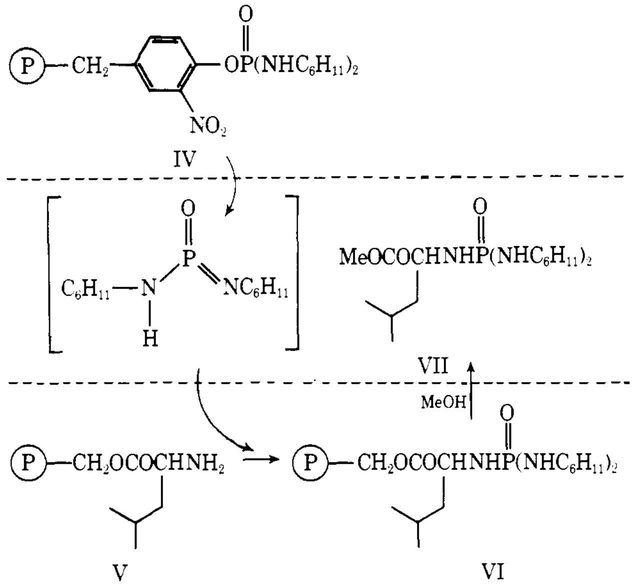
III

In a recent communication[11] we described an unambiguous test for reaction intermediates (Scheme I). The technique involves the generation of a reaction intermediate from an insoluble, polymer-bound precursor and its trapping on a second solid phase suspended in the same solution. Since the direct reaction of the two polymers is physically precluded, the formation of an adduct during the three-phase experiment requires the existence of a polymer-free intermediate. Application of the three-phase test for the detection of an intermediate in phosphorodiamidate transfer was accomplished as follows.

Scheme I



Scheme II



Macroreticular, cross-linked polystyrene (Rohm & Haas XE 305) was alkylated with 3-nitro-4-hydroxy benzyl chloride according to Patchornik's procedure,[12] and the resulting polymer-bound nitrophenol was phosphorylated with N,N-dicyclohexylphosphorodiamidic chloride to yield the precursor resin IV (Scheme II). The trapping agent V was prepared from chloromethylated polystyrene Merrifield's resin, Cal Biochem) by esterification to *tert*-butoxycarbonyl-L-leucine followed by N deblocking according to standard procedures.[13] When a suspension of IV and V in dioxane was treated with 1,8-bis(dimethylamino)naphthalene (proton sponge), phosphorodiamidate transfer could be detected on the resin VI (ir 1240 cm^{-1}). The adduct was removed from VI by dimethylaminoethanol-catalyzed transesterification to give VII, identical with an authentic sample.[14] Therefore, a phosphorylating agent must have been present in solution during the three-phase experiment.

While the existence of an intermediate is readily established, the structure of the phosphorylating agent cannot be specified with certainty. The isolation of a monophosphorylated product is consistent with the intermediacy of a monomeric metaphosphate, but dimers or oligomers of the metaphosphate cannot yet be excluded as the actual phosphorylating agent(s). It is unlikely that the phosphorylating agent is a phosphorylated proton sponge (i.e., nucleophilic catalysis of phosphate transfer) since this base has an extraordinary low nucleophilicity toward electrophiles other than protons.[15] Further, in full agreement with the predictions of Westheimer,[7c] no evidence for phosphate transfer could be found when the fully substituted VIII was used in place of IV during the three-phase test; thus an elimination-addition mechanism involving the metaphosphate (meta-