HIGHLY SELECTIVE TRITIUM-FROM-DEUTERIUM ISOTOPE SEPARATION BY PULSED NH_3 LASER MULTIPLE-PHOTON DISSOCIATION OF CHLOROFORM *

Frank MAGNOTTA, Irving P. HERMAN and Frederick T. ALDRIDGE
Department of Physics, University of California, Lawrence Livermore National Laboratory, Livermore, California 94550, USA

Infrared multiple-photon dissociation of $CTCl_3$ was investigated using a pulsed CO_2 laser-pumped NH_3 laser at 12.08 μm. No evidence of any $CDCl_3$ depletion or decomposition product was observed in photolyzed $CTCl_3/CDCl_3$ mixtures. A lower limit of the single-step T/D enrichment factor, β, was found to be ≈ 165, based on the sensitivity in measuring $CDCl_3$ depletion. The low-fluence $CTCl_3/CDCl_3$ optical selectivity in absorption is >9000 at the 835 cm^{-1} $CTCl_3$ ν_4 peak.

1. Introduction

The issue of removing the tritium content from tritium-contaminated coolant and moderator D_2O of a heavy water reactor must be satisfactorily addressed. One promising solution involves tritium-from-deuterium laser isotope separation of a hydrogen-bearing molecule that undergoes rapid T/D exchange with heavy water. This letter reports highly-selective decomposition of $CTCl_3$ from $CDCl_3$ by infrared multiple-photon dissociation (MPD) using a pulsed NH_3 laser, which is the first successful photochemical separation of tritium from deuterium. The described process may be even closer to practical implementation than the highly promising D/H [1–4] and T/H [5–7] separation schemes based on CO_2 laser photolysis of trifluoromethane.

Earlier normal mode calculation [7,8] of the $CTCl_3$ infrared spectrum suggested that the ν_4 mode would occur near 839 cm^{-1}, well removed from the $CDCl_3$ ν_4 (914 cm^{-1}) and ν_5 (774 cm^{-1}) fundamentals as well as from any $CDCl_3$ overtones, hot bands, or combination bands. $CTCl_3$ was synthesized and these spectroscopic expectations were confirmed. At 835 cm^{-1},

the measured $CTCl_3$ ν_4 peak, the absorption cross section of $CDCl_3$ is very small, and the ratio of the $CTCl_3$ absorption coefficient to that of $CDCl_3$, the isotopic selectivity, is found to be >9000 at 835 cm^{-1}. Since in the D/H separation by MPD of CHF_3 [2,4] and $CHCl_2CF_3$ [9], the single-step enrichment factor was observed to be greater than the low-fluence optical selectivity, the T/D enrichment factor here is expected to be >10000, unless isotopic scrambling of photolysis products with $CDCl_3$ is significant. $CTCl_3$ is found to readily decompose using the 12.08 μm (828 cm^{-1}) NH_3 laser line, while no evidence of any $CDCl_3$ decomposition is observed.

2. Experimental procedure

$CTCl_3$ was synthesized by base-catalyzed aqueous exchange between $CDCl_3$ and T_2O

$$CDCl_3 + T_2O \xrightarrow{\text{OD}^-} CTCl_3 + DTO \qquad (1)$$
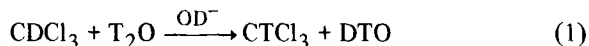
(0.21 ℓ/mole s for D/H at 20°C) [10]. A premeasured quantity of T_2 was passed over CuO wire at 450°C to produce $\approx 6 \times 10^{-3}$ cm^3 T_2O. $\approx 1 \times 10^{-3}$ cm^3 of 15 M NaOD in D_2O was preloaded into a 0.2 cm^3 stainless steel/glass thimble. Then ≈ 500 Torr cm^3 of $CDCl_3$ vapor and the T_2O were cryogenically transferred to

the thimble. These cited dimensions and quantities allowed a significant fraction of the chloroform and water to remain in the liquid phase to permit exchange; $CTCl_3$ production was accelerated via mixing by several freeze–thaw cycles. After exchange, the products were passed through molecular sieve 5A to remove the water, and were then analyzed by infrared spectroscopy and mass spectrometry. Typically, 20–70% of the chloroform was $CTCl_3$; the remainder was $CDCl_3$, with $\approx 2\%$ of $CHCl_3$. At times CCl_4 was observed in the tritiated samples due to radiolysis in high specific activity mixtures. The CCl_4 fraction increased noticeably after many weeks of storage. It was therefore preferable to dilute samples to the desired $CTCl_3/CDCl_3$ ratios immediately after $CTCl_3$ synthesis.

The grease-free main vacuum apparatus consisted of glassware, O-ring/glass plug/stopcocks, and stainless steel tubing and valves. The pyrex reaction cell (8.5 cm long, 1.3 cm i.d.), had KCl Brewster angle windows. After photolysis, the products were cryogenically transferred to the gas sampling valve loop of a temperature-programmed gas chromatograph. A 6 foot n-octane on porasil-C column was used for separation. The effluent of the gas chromatograph thermal conductivity detector was directly coupled to a 200 cm^3 ionization chamber.

Laser photolysis of $CTCl_3$ was monitored by a decrease in the ionization chamber output, as compared to an unphotolyzed sample; depletion of $CDCl_3$ was similarly monitored by the thermal conductivity detector. Run-to-run variations in the detection of identical quantities of a molecule were typically ±3%. In some cases $\approx 2\%$ of c-C_4F_8 was added to $CTCl_3/CDCl_3$ mixtures for internal calibration.

A 0.3 Hz repetition rate, pulsed CO_2 laser delivering 4 J at R(30), 9.22 μm in a 100 ns fwhm pulse was coupled off a grating into a 120 cm long cell filled with 1 Torr NH_3/20 Torr N_2. The ammonia laser resonator consisted of this grating, a totally reflecting 15 m radius concave mirror (in the cell arm), and a partially reflective (ranging from 35–80% reflecting) 10 m concave output mirror [11]. Typical operating characteristics were 350 mJ output in 1.5 μs fwhm pulses at the 12.08 μm [828 cm^{-1}, sP(7, K)] line used. No radiation (<0.1%) was observed near 11.7, 12.0, 12.3 and 12.5 μm, which are the strongest wavelengths of NH_3 superradiant emission. The 12.08 μm pulse was focused into the center of the reaction cell by either a 25 or 50 cm focal length KCl lens.

In some cases, the photolyzing fluence was doubled by retroflecting the transmitted beam with a totally reflecting concave mirror, with radius of curvature approximately equal to the lens focal length, placed a distance of one lens focal length past the cell focus. In such cases, the effectively-doubled laser energy per pulse incident on the cell is cited as the net incident energy. This retroreflection did not couple back into the NH_3 laser.

3. Results

The infrared spectrum of a typical $CTCl_3/CDCl_3$ gas mixture is shown in fig. 1. The $CTCl_3$ ν_4 peak occurs at 835.3 ± 0.3 cm^{-1} and ν_5 at 674 cm^{-1}, as predicted by the normal mode calculations, with the Ruoff and Burger [12] force field providing the best spectral fit. There is no discernable infrared absorption in 1800 Torr cm path lengths in $CDCl_3$ from 815–842 cm^{-1} [$<8^{+3}_{-8} \times 10^{-6}$/cm Torr].

The low-fluence absorption coefficient at the peak of ν_4 $CTCl_3$ was determined from the known (and remeasured) $CDCl_3$ absorption coefficient, the $CTCl_3/CDCl_3$ infrared spectrum, and the mass spectrometric measurement of $CTCl_3/CDCl_3$ concentration ratio of each sample. It is $(10.2 \pm 0.7) \times 10^{-2}$/cm Torr, 1.6 times that of the ν_4 mode in $CDCl_3$. The low-fluence optical selectivity for $CTCl_3/CDCl_3$ at 835 cm^{-1} is $12000^{+\infty}_{-3000}$, while at the ammonia laser photon energy, 828 cm^{-1}, it is $6500^{+\infty}_{-1900}$.

When $CTCl_3$ was irradiated by 12.08 μm, a large,
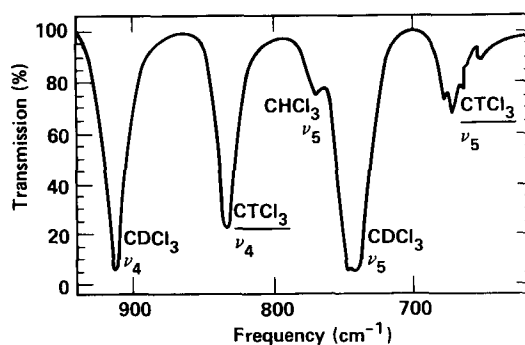

Fig. 1. The infrared spectrum of $CTCl_3$ synthesized by $CDCl_3$/T_2O/OD^- exchange. In this undiluted sample $\approx 25\%$ of the chloroform is tritiated.

highly selective depletion of $CTCl_3$ occurred, though, in no case did any tritiated product appear in the ionization chamber due to laser photolysis. In some samples, small amounts (ppm level) of tritiated impurities, such as dichloromethane and trichloroethylene, and non-tritiated products ($\ll 0.1\%$), such as carbon tetrachloride and dichloromethane, were present in equal quantities in photolyzed and null samples. Since the absolute quantities of irradiated $CTCl_3$ were purposely kept small, no $CTCl_3$ product was expected or appeared using the thermal conductivity detector. No $CDCl_3$ reactant depletion (within $\approx \pm 3\%$) or $CDCl_3$ decomposition products were observed with 12.08 μm laser irradiation.

The extent of $CTCl_3$ and $CDCl_3$ reagent depletion versus the number of irradiating pulses is shown in fig. 2. In the 25 cm focus plots of remaining $CTCl_3$ and $CDCl_3$, a net of 460 mJ per pulse irradiated the

Fig. 3. $CTCl_3$ decomposition versus laser pulse energy (200 mTorr, 200 ppm T/D, 50 cm focal length lens).
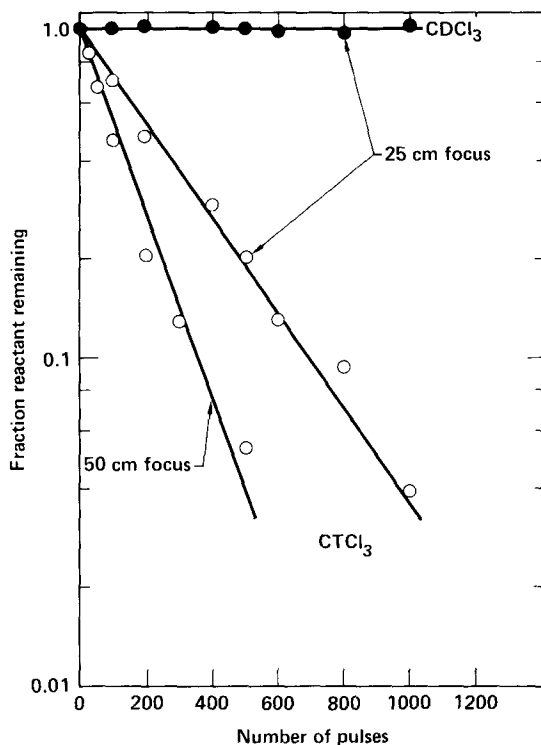

Fig. 2. Reactant depletion versus number of irradiating pulses for $CTCl_3$ and $CDCl_3$ with a 25 cm focus with retroreflection (200 mTorr, 200 ppm T/D, 460 mJ net pulse energy), and for $CTCl_3$ with a 50 cm focus (200 mTorr, η = 200 ppm, 505 mJ net laser pulse energy).
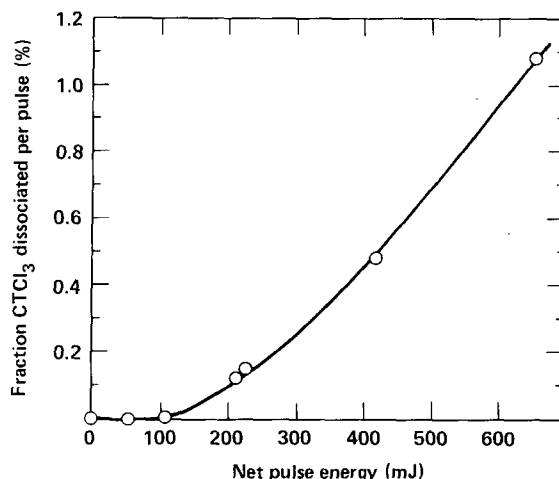
cell (including retroflection); the 200 mTorr chloroform sample had T/D ratio, η, of 200 ppm. A 50 cm focal length lens focused a net of 505 mJ per pulse of 12.08 μm radiation into the cell containing 200 mTorr with η = 200 ppm in the 50 cm focus $CTCl_3$ curves. For the 25 cm focusing case 0.32% of the present $CTCl_3$ decomposed per shot. Based on the 2.0% standard deviation from the best fit line in the $CDCl_3$ plot (which is horizontal), $CDCl_3$ depletion per shot is $< 2.0 \times 10^{-5}$.

The laser pulse energy dependence of infrared photolysis of the $CTCl_3$ in 200 mTorr with η = 200 ppm (50 cm lens) is shown in fig. 3, data being taken both with and without retroreflection. This plot depicts the fractional decomposition of the cell contents per shot. The laser swept $\approx 2.5\%$ of the cell volume. With 400 mJ of energy incident on the cell, the fluence near the focus was ≈ 20 J/cm^2, while at the windows it was ≈ 6 J/cm^2.

Fig. 4 portrays the dependence of $CTCl_3$ dissociation on added $CDCl_3$. The fractional decomposition per pulse is shown for 50 cm focal length optics with 270 mJ incident (one-pass) and a net of 535 mJ in the cell (retroreflection). For all data the $CTCl_3$ partial pressure was $\leqslant 0.15$ mTorr, so $CTCl_3 - CTCl_3$ collisions are unimportant. For the 270 mJ data, T/D was fixed at 195 ppm for $CDCl_3$ pressures below 0.75 Torr and at 19 ppm above 0.75 Torr. For the 535 mJ data, η = 150 ppm for total pressures below 0.75 Torr and 24
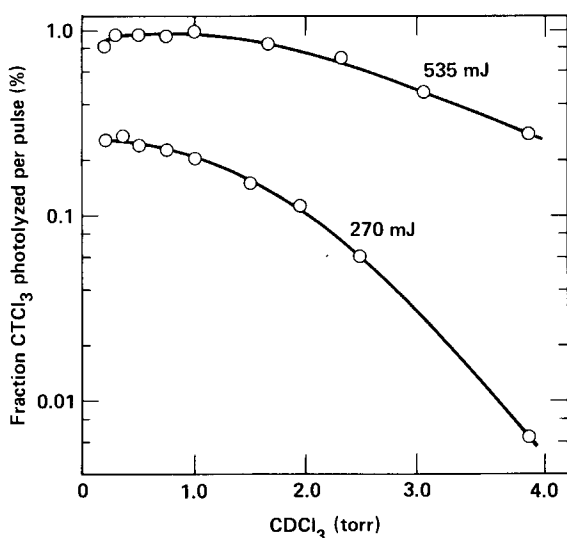
Fig. 4. $CTCl_3$ dissociation probability versus added $CDCl_3$ with either 270 mJ or a net 535 mJ per pulse incident (see text for details).

ppm at higher pressures. The $CTCl_3$ dissociation probability is quenched to one half its low pressure value with 1.7 Torr of added $CDCl_3$ when 270 mJ is incident, and with 3.0 Torr $CDCl_3$ when 535 mJ impinges on the cell.

Several more 12 μm laser experiments on $CTCl_3$/ $CDCl_3$ mixtures and neat $CDCl_3$ were performed, similar to those described above except many more pulses irradiated the sample in order to search for $CDCl_3$ decomposition; no $CDCl_3$ photolysis products were detected.

Infrared multiple-photon dissociation of $CDCl_3$ was also studied, using the CO_2 laser P(48), 10.91 μm line to pump the $CDCl_3$ ν_4 mode. The relevant major findings are presented here; details will be published elsewhere. For $CDCl_3$ pressures below 1 Torr, C_2Cl_4 was the main carbon-containing product, while C_2Cl_2, CCl_4, and C_2DCl_3, were minor products. Trichloroethylene was apparently due to wall reactions, since this product decreased with reaction cell seasoning and, in fact, totally disappeared with the addition of 50 Torr argon buffer — though reagent depletion remained the same in both cases. Only by using large reaction vessels (300 cm^3 volume) and $CDCl_3$ pressures over 1 Torr could enough of the reactive deuterium chloride be formed to be observed on the thermal conductivity detector. This explains why no TCl, the ma- ᵣ

jor tritium-bearing product, was observed in the ionization chamber traces here.

Since no $CDCl_3$ photolysis products were ever seen with 12 μm photolysis, the system collection capability of small amounts of products was tested. 200 mTorr C_2Cl_4/$CDCl_3$ mixtures were placed in the reaction cell, and then transferred to the gas chromatograph; C_2Cl_4 mole fractions down to the lowest measured point of 0.1% were easily seen. Studies of the 10.91 μm photolysis of 200 mTorr $CDCl_3$ in the same 14 cm^3 volume reaction cell showed that <1% deuterated chloroform conversion to any product should have been seen. For experiments at higher pressure, smaller conversion can be observed; for instance, it was confirmed that at 2 Torr total pressure (as in fig. 4), <0.1% product formation from $CDCl_3$ decomposition is detectable.

4. Discussion

The determination of the nascent and subsequent steps of chloroform pyrolysis has been the subject of numerous investigations for over forty years. Both flow and shock-tube techniques have been employed, using various types of isotopic scavengers and detection methods to resolve the kinetics. Still, these studies do not definitively conclude whether hydrogen chloride [13–16] or chlorine atom [17,18] elimination (or both) is the nascent step,

$$CTCl_3 \rightarrow :CCl_2 + TCl , \qquad (2)$$

$$CTCl_3 \rightarrow \cdot CTCl_2 + Cl . \qquad (3)$$

In the most recent shock tube study of $CHCl_3$ pyrolysis [16], reaction (2) is claimed to be the nascent step, with a measured activation energy of 54.5 ± 2.9 kcal/ mole. Based on the latest measured enthalpy of CCl_2, 53.5 ± 2.3 kcal/mole [19], reaction (2) is 56 kcal/ mole endoergic. A typical barrier for a three-center hydrogen chloride elimination back reaction in a halogenated methane is ≈6 kcal/mole [20], so reaction (2) should have an activation energy of 62 kcal/mole, significantly higher than the measured value; that of reaction (3) should be ≈70 kcal/mole [13]. According to quantum RRK theory, $CTCl_3$ molecules excited ≈8 kcal/mole above the dissociation energy decompose by reaction (2) in ≈5 ns, slow enough for (2) and (3) to be competitive.

The appearance of large amounts of C_2Cl_4 in $CDCl_3$ IR laser photolysis suggests the contribution of eq. (2) through:

$$:CCl_2 + :CCl_2 \rightarrow C_2Cl_4 \qquad (4)$$

or

$$:CCl_2 + CDCl_3 \rightarrow C_2Cl_4 + DCl . \qquad (5)$$
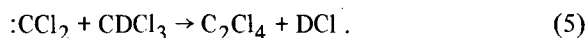
Since CCl_4, though not C_2Cl_4 at room temperature can be formed as a result of reaction (3) [17,18], apparently both (2) and (3) are important. Depending on the route of C_2Cl_4 formation [(4) or (5)], C_2Cl_2 may be formed by $Cl + Cl$ or Cl_2 elimination or by secondary photolysis (only in the 10.9 μm studies). In the $CTCl_3/CDCl_3$ experiments there was no evidence for $TCl/CDCl_3$ isotope scrambling.

The fluence dependence observed in fig. 3 is consistent with a multiple-photon dissociation probability that rises as the 2.5 ± 0.5 power of the local fluence until it reaches unity at and stays at unity above the saturation fluence of $\approx 23 \pm 3$ J/cm^2.

In this study, the 12.08 μm line of the ammonia laser was used since it is red-shifted 7 cm^{-1} from the $CTCl_3$ ν_4 peak, and the red-shift in the ν_4 ladder is large. The X_{44} anharmonicity constant for ν_4 in $CTCl_3$ is estimated to be -8.9 cm^{-1}, using Dennison's isotope shifting rule and X_{44} measured in $CDCl_3$ [21].

The single-step T/D enrichment factor, β, is defined as the ratio of the fractional $CTCl_3$ decomposition per pulse, σ_T, to that of $CDCl_3$, σ_D. From the short-focus data of fig. 2 ($\eta = 200$ ppm), β is conservatively >165, limited by the uncertainty in the run-to-run $CDCl_3$ reagent depletion measurements. Higher lower-limit estimates come from the fact that no products ever appeared, although for runs at 2 Torr it is estimated that products arising from 0.1% $CDCl_3$ decomposition would have been observed. Data near 2 Torr $CDCl_3$ in fig. 4 (75 pulses, 535 mJ) suggest $\beta > 540$; similar experiments with more pulses (250 pulses, 570 mJ) puts $\beta > 2200$. (In these cases, 42% and 89% of initial $CTCl_3$ was decomposed.) It should be noted that these two values are quite sensitive to the minimum detectable product.

There are three important modes of $CDCl_3$ decomposition with 12 μm irradiation: (1) direct MPD (possibly assisted by $CDCl_3-CDCl_3$ collisions), (2) MPD after collisional excitation by hot $CTCl_3$, and (3) reaction with $CTCl_3$ dissociation products. For the last

two cases σ_D is proportional to the $CTCl_3$ partial pressure. (Of course, if these two mechanism were significant, the above-cited lower limits for β would actually correspond to mixtures with η somewhat smaller than the pre-photolysis values.)

Since $CDCl_3$ is highly transparent near 12.08 μm, direct MPD cannot be very important. If only direct MPD leads to $CDCl_3$ dissociation, β should be greater than the high fluence optical selectivity; however, previous studies have shown that β can be even larger than the low fluence optical selectivity [2,4,9] ($\geqslant 4600$ at 828 cm^{-1}). In experiments in which 2800 pulses of 12 μm were incident on neat $CDCl_3$ (1 Torr, net 520 mJ, 50 cm focus) there was still no evidence of $CDCl_3$ depletion or products; in the worst case these data imply $\beta \gg 400$ if only direct MPD is important.

If $\beta = 160$ (fig. 2, 25 cm focus, 200 mTorr, $\eta = 200$ ppm) and if σ_D were $CTCl_3$ dependent, then ≈ 30 $CDCl_3$ would be lost per removed $CTCl_3$. Since there are only ≈ 5 $CTCl_3-CDCl_3$ collisions during the laser pulse under these conditions, and since at room temperature there is no apparent mechanism for a chain reaction [though for (2) or (3) one $CDCl_3$ may decompose per $CTCl_3$, as in (5)], neither $CTCl_3$-dependent σ_D mode can support such a small β. (Still, if σ_D depends linearly on η, and $\beta(\eta = 200$ ppm$) = 160$, then at the typical heavy water reactor T/D value of 5 ppm, β would be ≈ 6400.)

Studies presently being conducted will characterise the spectral dependence of $CTCl_3$ MPD, examine the nascent MPD reaction and the subsequent chemistry, and more precisely determine the large tritium enrichment factor.

References

[1] I.P. Herman and J.B. Marling, Chem. Phys. Letters 64 (1979) 75.

[2] I.P. Herman and J.B. Marling, J. Chem. Phys. 72 (1980) 516.

[3] J.B. Marling, I.P. Herman and S.J. Thomas, J. Chem. Phys. 72 (1980) 5603.

[4] S.A. Tuccio and A. Hartford Jr., Chem. Phys. Letters 65 (1979) 234.

[5] Y. Makide, S. Hagiwara, T. Tominaga, K. Takeuchi and R. Nakane, Chem. Phys. Letters 82 (1981) 18.

[6] K. Takeuchi, I. Inoue, R. Nakane, Y. Makide, S. Kato and T. Tominaga, J. Chem. Phys. 76 (1982) 398.

[7] I.P. Herman and J.B. Marling, J. Phys. Chem. 85 (1981) 493.

[8] I.P. Herman and J.B. Marling, Lawrence Livermore National Laboratory, Livermore, CA 94550, UCID-18509-79-4 (January 1980), unpublished, available from NTIS.

[9] J.B. Marling and I.P. Herman, Appl. Phys. Letters 34 (1979) 439.

[10] J. Hine, R.C. Peak Jr. and B.D. Oakes, J. Am. Chem. Soc. 76 (1954) 827.

[11] H. Tashiro, K. Suzuki, K. Toyoda and S. Namba, Appl. Phys. 21 (1980) 237, and references therein.

[12] A. Ruoff and H. Burger, Spectrochim. Acta 26A (1970) 989.

[13] A.E. Shilov and R.D. Sabirova, Russian J. Phys. Chem. 34 (1960) 408.

[14] J.W. Engelsma, Rec. Trav. Chim. 84 (1965) 187.

[15] S.W. Benson and G.N. Spokes, 11th Symp. Intern. Combustion (1967) p. 95.

[16] K.P. Schug, H.Gg. Wagner and F. Zabel, Ber. Bunsenges. Physik. Chem. 83 (1979) 167.

[17] G.P. Semeluk and R.B. Bernstein, J. Am. Chem. Soc. 76 (1954) 3794; 79 (1957) 46.

[18] T. Yano, Bull. Chem. Soc. Japan 50 (1977) 1272.

[19] B.A. Levi, R.W. Taft and W.J. Hehre, J. Am. Chem. Soc. 99 (1977) 8454.

[20] Aa.S. Sudbo, P.A. Schulz, Y.R. Shen and Y.T. Lee, J. Chem. Phys. 69 (1978) 2312.

[21] M.V. Garcia, R. Escribano, G. Del Rio and J.M. Orza, Anal. Quim. 71 (1975) 745.