CO_2 LASER-INDUCED DECOMPOSITION OF METHYL IODIDE SENSITIZED BY SULFUR HEXAFLUORIDE*

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Gaseous mixtures of methyl iodide and sulfur hexafluoride yield upon irradiation by a continuous-wave CO_2 laser iodine, methane, ethane, ethylene and acetylene — the products of methyl iodide decomposition. The decomposition rate and the mutual ratio of the products is dependent on the delivered irradiation energy, the methyl iodide/sulfur hexafluoride ratio and the energy of the exciting photon. Methyl iodide-d_3 in the mixture with SF_6 behaves similarly as methyl iodide yielding perdeuterated methane, ethane, ethylene, acetylene and iodine.

This work reports on the behaviour of methyl iodide upon irradiation by a continuous-wave CO_2 laser. Methyl iodide itself can serve as active medium of both an optically pumped laser emitting radiation in the submillimeter region[1] and a laser operating[2] on the basis of the CH_3I photodissociation. If this compound is excited by a Q--switched CO_2 laser, infrared fluorescence[3] is observed and by means of it methyl iodide can be detected[4] even in nanogram concentrations.

Methyl iodide decomposes also upon the ultraviolet irradiation. Owing to its continuous absorption with a maximum at 250 nm the irradiation beam from a low-pressure mercury discharge lamp ($\lambda = 253{\cdot}7$ or 185 nm) brings about the methyl iodide decomposition in both the liquid[5] and gaseous[6-10] state. Photolysis[11-14], radiolysis[15-17] and flash-photolysis[18] produce methyl radicals and excited atomic iodine, whose further fates are controlled by media in which the decomposition occurs and by the kinetic energy acquired in the course of the excitation. The major product of reactions of the methyl radical is preponderantly methane; other reaction products are ethane or ethylene and iodosubstituted methanes.

Methyl iodide has, however, been shown to be stable upon irradiation by a CO_2 laser. Despite that the ${}^RQ_6$ line of the ν_6 rotational-vibrational band[19] of methyl iodide ($932{\cdot}87\ cm^{-1}$) almost coincides with the $P(32)$ line ($00^01 \rightarrow 10^00$ transition) of the CO_2 laser ($932{\cdot}96\ cm^{-1}$), no decomposition was observed when this (or another line of the same transition of the CO_2 laser) was chosen for the irradiation. The stability of methyl iodide is not influenced by admixtures of other halogenated methanes, but it is affected by the addition of sulfur hexafluoride. When the mixture of CH_3I and SF_6 is irradiated, a very fast decomposition of methyl iodide occurs yielding elementary iodine, methane, ethane, ethylene and acetylene. The decomposition rate and the product ratio is dependent on many variables of the procedure. No iodine-containing compounds were found among the reaction products.

This work presents a study of the CO_2 laser initiated decomposition of methyl iodide, methyl iodide-d_3 and the methyl iodide/methyl iodide-d_3 mixtures in the presence of sulfur hexafluoride. On the basis of the experimental data a mechanism for the methyl iodide decomposition is suggested.

EXPERIMENTAL

For the irradiation of methyl iodide and its mixtures (with SF_6 or halogenated methanes) a cw CO_2—N_2—He laser constructed[20] in our laboratory and adjusted for this purpose was used. The laser resonator consisted of a mirror with total reflection and a difraction grating (81 groves per mm) by means of which individual lines of the laser transitions were selected. The $P(14)$ ($\nu = 949{\cdot}48\ \text{cm}^{-1}$) to $P(46)$ ($\nu = 918{\cdot}72\ \text{cm}^{-1}$) lines of the $00^01 \rightarrow 10^00$ transition were used in the irradiation. The laser power obtained with the individual lines did not surpass 35 W. Samples were irradiated in gas cells (C. Zeiss, Jena) of 10 cm optical path length. The spectroscopic cells with the transparent sodium chloride or potassium bromide windows were filled before irradiation with the gaseous mixture. Unless otherwise specified, the pressure of methyl iodide did not exceed in all the experiments 6·7 kPa. The composition of the gaseous mixtures was followed before irradiation, in the course of the decomposition, and after the decomposition by IR spectroscopy. The IR spectra were recorded on the Perkin–Elmer spectrophotometer Model 621. When IR spectra were used to assess the amounts of arising products (methane, acetylene), the absorptivity needed were obtained from the spectra of pure compounds. Analysis of the reaction products was performed by a GLC (Chromatograph Chrom 3, Laboratorní přístroje) with columns packed with silica gel.

In order to compare the decomposition course under the laser irradiation with the influence of heat, the static pyrolysis of methyl iodide and its mixture with SF_6 was performed in a quartz tube of 40 cm length and 2 cm diameter with a run time of 10 s.

Methyl iodide (*p.a.*, Lachema, Brno) and sulfur hexafluoride (I.E.C. Standard, Montedison Milano) were commercial products and methyl iodide-d_3 was kindly supplied by the Laboratory of Isotopes Institutes of Biology, Czechoslovak Academy of Sciences, Prague-Krč.

RESULTS AND DISCUSSION

In the region of the CO_2 laser emission gaseous methyl iodide shows a bunch of Q-branches of the ν_6 rotational-vibrational band, some components[14] of which almost coincide with the CO_2 laser lines (${}^RQ_8$ $949{\cdot}20\ \text{cm}^{-1}$ with the $P(14)$ line at $949{\cdot}48\ \text{cm}^{-1}$, ${}^RQ_6$ $932{\cdot}87\ \text{cm}^{-1}$ with the $P(32)$ line at $932{\cdot}96\ \text{cm}^{-1}$ and ${}^RQ_5$ $924{\cdot}83\ \text{cm}^{-1}$ with the $P(40)$ line at $924{\cdot}98\ \text{cm}^{-2}$). On the irradiation of gaseous CH_3I with the CO_2 laser beam the radiation is evidently absorbed[1,3,4]. However, no CH_3I decomposition occurred under these conditions even after 10 minutes of irradiation of the gaseous CH_3I (6·7 kPa) by a focussed laser beam (various $00^\circ1 \rightarrow 10^\circ0$ transition lines around $P(32)$, power 35 W). The absorption bands of CH_3I vibrations (strong bands of ν_1 vibration at 2983 (R-branch) and 2961 (P-branch), ν_2 vibration at 1 264 (R), 1 253 (Q) and 1 242 (P) cm^{-1}, weaker bands at 2860 cm^{-1}, perpendicular bands of ν_4, ν_5 and ν_6 vibrations centered at 3060, 1 435 and 882 cm^{-1}) did not show any intensity change after the experiments were terminated.

However, a different behaviour of methyl iodide was observed when sulfur hexafluoride was added. An almost complete decomposition of methyl iodide was achieved by the irradiation of the CH_3I/SF_6 mixture ($P(32)$ line, 34 W power, unfocussed beam) after the period of 1 minute. With the focussed beam the decomposition proceeds much faster.

During the irradiation of the CH_3I/SF_6 mixture a brightly red fluorescence appears in the reaction zone, whose intensity decreases with the irradiation time. Immediately after the irradiation starts (*e.g.* as early as after 1 s) iodine is formed (as a vapor and crystals deposited on the cell walls and on the entrance window) along with methane (intense Q-branches of ν_3 and ν_4 rotational-vibrational bands at 3019 and 1306 cm^{-1}) and acetylene (very intense Q-branch of ν_5 band at 730 cm^{-1}). The intensity of the vibrational bands of methyl iodide declines as the decomposition grows more significant, but the absorption bands[21] belonging to sulfur hexafluoride diminish their intensity only in a negligible extent (less than 1%, result of many measurements), since sulfur hexafluoride acts only as a sensitizer and does not otherwise participate in the decomposition. The decrease of the SF_6 amount is related to the side reaction of SF_6 with the cell glass[22] surface as follows from the appearance of the bands of SiF_4 (ν_3 at 1031 cm^{-1}) and SOF_2 (ν_1, ν_2 and ν_5 at 1333, 809 and 720 cm^{-1}, respectively). Furthermore, in such instances when air penetrated into the cell during the experiment, typical rotational-vibrational bands of CO and CO_2 arise in the spectra of the decomposition product mixture, too.

Upon irradiation of the CH_3I/SF_6 mixture (pressure ratio 6·7/2·7 kPa) by the $P(34)$ line (931·00 cm^{-1}) by the laser output of 28 W the decomposition of methyl iodide was finished as early as after 2 minutes. Iodine was observed in the cell, the bands of CH_3I disappeared, and those of methane (the intensity of the ν_3 band corresponds roughly to 3·5 kPa of methane) and acetylene (on the basis of the intensity of the ν_5 band the amount of acetylene assessed is 0·64 kPa) appeared. GLC showed methane, ethylene and acetylene in the mixture of products in the ratio 8 : 1 : 1, respectively. Further irradiation of the mixture did not bring about any marked changes in composition.

Let us attempt to write the reaction balance for the case when the decomposition of methyl iodide is complete. First, it is neccesary to state that the decomposition products (except of iodine) are gaseous, and solid carbon (a frequent product of pyrolytic reactions carried out at high temperatures) is not formed. In attempting to write stoichiometric equation describing the methane, ethylene and acetylene (and iodine) formation from methyl iodide we arrived at equation (*A*):

$$10\,CH_3I = 5\,I_2 + 6\,CH_4 + C_2H_4 + C_2H_2\,. \tag{A}$$

According to this scheme 6·7 kPa of methyl iodide should yield 4 kPa of methane, whereas 3·5 kPa of methane was estimated from IR spectra; the acetylene yield ought to be 0·67 kPa and 0·64 kPa was found. With regard to the accuracy of the analytical method used and the experimental set-up, the match between the calculated and found values is satisfactory. If we had not some knowledge on the decomposition of methyl iodide d_3, the difference between 8 : 1 : 1 (the ratio $CH_4 : C_2H_4 : C_2H_2$ obtained from the GLC analysis) and 6 : 1 : 1 (equation (*A*)) ratios should have been ascribed to some inaccuracies of the analytical procedures. However, methyl iodide-d_3 gives the following compounds upon its laser induced decomposition: CD_4, C_2D_4, C_2D_2 and iodine (all these products are analogous to the products of the CH_3I decomposition) and CD_3H (weak band of the ν_6 vibration at $1036\,cm^{-1}$). The hydrogen needed to the formation of the last compound was likely provided by the OH groups of the glass cell surface, similarly as in the case of the same contamination[23] from the surface of ZnO. Despite the fact that the amount of CD_3H formed by the decomposition of CD_3I is small, it proves the possibility for the hydrogen balance disruption due to the hydrogen source outside the Eq. (*A*).

Formation of Methane and Ethane

In order to explain the formation of methane on the CH_3I decomposition in the presence of SF_6 initiated by the irradiation from the CO_2 laser, we have, first of all, to presume a vibrational excitation of SF_6 molecules and their ensuing interaction with molecules of CH_3I. The $V-T$ type of relaxation for the SF_6 molecules has to be suggested[24], too, so that the molecules of methyl iodide can enter into the interaction with either vibrationally excited, or translationally "hot" molecules of SF_6. In any case, the reaction (*B*) can be postulated as the first decomposition stage

$$SF_6^* + CH_3I \rightarrow SF_6 + CH_3^{\bullet} + I^{\bullet}\,. \tag{B}$$

The abstraction reaction (*C*) necessitates, however, "hot" methyl

$$CH_3^{\bullet} + CH_3I \rightarrow CH_4 + CH_2I^{\bullet} \tag{C}$$

radicals[6,7] (of a high kinetic energy). As Table I shows, the methane content in the mixture of decomposition products increases with the growing laser output (experiments 1–3). The methyl radicals arising in process (*B*) can increase their kinetic energy by chemically inert collisions with "hot" molecules of SF_6 just as the laser output grows.

On the contrary, methyl radicals having an insufficient kinetic energy can be rather presumed to undergo recombination[6]. The recombination product is ethane formed according to the scheme (*D*)

$$CH_3^{\bullet} + CH_3^{\bullet} + M \rightarrow C_2H_6 + M\,, \qquad (D)$$

where M designates molecules of the moderator. This type of recombination was ascertained in our experiments just when irradiation with low outputs was used. The largest amount of ethane (23%) was formed under irradiation of the CH_3I/SF_6 mixtures with laser power of 6 W (Table I, exp. 1), however, conversion of the CH_3I decomposition was rather low (15%). The decomposition of CH_3I in the presence of SF_6 is, certainly, the threshold reaction and when the *P*(32) or *P*(34) line with the output $\leqq 2$ W are used for the irradiation, it did not occur at all.

The hypothesis of the methyl radical formation under the CH_3I decomposition is supported by results on the decomposition of the $CH_3I/CD_3I/SF_6$ mixture with varying CH_3I/CD_3I ratio 5·4 : 1·4, 3·3 : 3·3 and 1·4 : 5·4 (in kPa). The IR spectra of the decomposition products revealed isotopomers of methane CH_4, CH_3D (the bands of ν_2 and ν_6 vibrations at 2202 and 1155 cm^{-1}, respectively), CHD_3 (the

TABLE I

Basic Data on the CH_3I/SF_6[a] Decomposition Initiated by the CO_2 Laser Radiation

Exp.	Used line no	Used line output W	Run time s	Conversion[b] %	Products[c] mol % CH_4	C_2H_6	C_2H_4	C_2H_2	Methane kPa[d]	Methane kPa[c]
1	*P*(32)	6	30	15	44	23	33	0	0·37	0·44
2	*P*(32)	12	30	35	54	15	30	1	1·41	1·27
3	*P*(32)	20	30	70	70	1	12	6	2·85	3·24
4	*P*(32)	12	2	10	60	5	35	0	0·32	0·36
5	*P*(32)	12	10	23	65	9	24	2	1·12	1·00
6	*P*(32)	12	60	65	76	3	18	3	3·33	3·69
7	*P*(20)	12	300	40	60	17	23	0		
8	*P*(30)	12	300	75	70	4	24	2		
9	*P*(40)	12	300	90	80	2	14	4		

[a] Pressure of both CH_3I and SF_6 in cell before the irradiation was always 6·7 and 2·7 kPa, respectively; [b] the percentage of methyl iodide decomposed; [c] based upon GLC analysis; [d] calculated from the intensity of ν_4 vibrational band.

bands of ν_1 and ν_6 vibrations at 2993 and 1036 cm^{-1}, respectively) and CD_4 (the bands of ν_3 and ν_4 vibrations at 2260 and 996 cm^{-1}, respectively). Their formation is due to the reactions described by schemes similar to Eq. (*C*) in which $CH_3^{\bullet}$ and $CD_3^{\bullet}$ radicals react with CH_3I and CD_3I. The isotopomers content corresponds to the CH_3I/CD_3I ratio before the decompositions were initiated. The IR spectra never showed the presence of methane-d_2 among the reaction products when the CH_3I/CD_3I mixture in the 3·3 : 3·3 (in kPa) ration was irradiated. Its occurrence in the reaction products mixture would manifest a mere statistical H/D distribution in the system of reacting components.

Formation of Ethylene and Acetylene

Both methane and ethane seem to be products arising from methyl radicals generated from methyl iodide according to Eq. (*B*). Formation of ethylene is related to another precursor, the $CH_2I^{\bullet}$ particle[6,10], arising simultaneously with methane in process (*C*). As Table I shows, ethylene is formed in a great amount (experiment 1 – 33%) already upon the irradiation of methyl iodide with low laser power. With the increasing laser power (and the irradiation time) its content slowly decreases.

Ethylene can be produced by the decomposition of ethylene iodide Eq. (*E*) (the process does not require a high activation energy[25])

$$ICH_2CH_2I \rightarrow C_2H_4 + I_2 \tag{E}$$

formed by the recombination of the $CH_2I^{\bullet}$ species[6] as described by Eq. (*F*). The CHI particle was considered to participate in the CH_3I decomposition by a hot process[17] and by UV radiation[26];

$$CH_2I^{\bullet} + CH_2I^{\bullet} + M \rightarrow ICH_2CH_2I + M \tag{F}$$

sometimes the CH_2 particle[27,28] and even the CH particle[29] are taken into account. Their recombination (and possibly other reaction) are used in order to explain the ethylene and acetylene formation. The secondary source of ethylene (and that of methane and acetylene, too) can be provided by the $CH_3^{\bullet}$ radical (Eq. (*D*)). As we have found, ethane is decomposed very rapidly (giving the mixture of hydrocarbons[20]) in the presence of SF_6 under conditions similar to those under which the CH_3I decomposition takes place. However, ethane cannot, at no rate, be considered as a major source of ethylene. Acetylene is a typical product of abstraction processes most probably inciated by the methyl radical. To take into account other abstraction reactions of the $CH_3^{\bullet}$ radical that, in accordance with its kinetic energy content, will be able to abstract hydrogen (and form methane) not only from methyl iodide but also from other molecules and particles in the reaction zone, is, therefore, necessary.

The apparent formation of compounds with two carbon atoms from the methyl radical turns out from the IR spectral analysis of reaction products obtained by the irradiation of the $CH_3I/CD_3I/SF_6$ mixture with a variable CH_3I and CD_3I content. The absorption bands of ν_5 vibrations of the isotopomers $HC{\equiv}CH$, $HC{\equiv}CD$ and $DC{\equiv}CD$ at 730, 678 and 537 cm^{-1}, respectively, and the absorption bands of the ν_7 vibration of the isotopomers $H_2C{=}CD_2$ and $D_2C{=}CD_2$ at 752 and 720 cm^{-1}, respectively, were found (the ν_7 vibrational band of ethylene centered at 949 cm^{-1} coincides with a vibrational band of SF_6). The comparison of the band intensities for the $H_2C{=}CD_2/D_2C{=}CD_2$ and $HC{\equiv}CH/HC{\equiv}CD$ pairs in mixtures of the reaction products of a different CH_3I/CD_3I ratio speaks in favor of the statistically accidental H/D distribution in the decomposition products.

Formation of Iodine

As scheme (*B*) describes, atomic iodine arises in the methyl iodide decomposition, too. From the experiments dealing with the methyl iodide decomposition by ultraviolet irradiation the iodine turned out to be liberated in the $I(5^2P_{1/2})$ excited state[6]; with regard to other similarities of our experiment with the decomposition iniciated by UV radiation, we suggest the occurrence of the excited atomic iodine also in our experiment. Its relaxation by a spontaneous emission in the visible region could offer a simple explanation for an intense fluorescence accompanying the CH_3I decomposition. The most significant reaction of atomic iodine is its recombination which produces molecular iodine. The excited iodine exerts a pronounced ability for abstraction reactions and its exothermic reaction[31] with methyl iodide according to Eq. (*G*) is known. However, this process can result only in a change of the

$$I(5^2P_{1/2}) + CH_3I \rightarrow I_2 + CH_3^{\bullet} \qquad (G)$$

reaction rate, and similarly the processes (*H*) and (*I*), does not influence the reaction product composition.

$$CH_3^{\bullet} + I \rightarrow CH_3I \qquad (H)$$

$$CH_3^{\bullet} + I_2 \rightarrow CH_3I + I\,. \qquad (I)$$

We have studied the reaction course of the methyl iodide decomposition under such conditions, when the iodine formed during the reaction was scavenged by silver deposited on a glass tube inserted into the cell. The iodine generated was, at least at the very beginning, bound on the silver layer. After five minutes of irradiation by the *P*(34) line with 12 W output the conversion of the methyl iodide decomposition was observed. The GLC analysis of the product composition revealed (in molar percent) methane (87), ethane(1), ethylene (10·5) and acetylene (1·5). The result significantly differs from that found for the CH_3I decomposition by ultraviolet irradiation in the presence of silver when ethane was a major product[6,32] (it was produced in an amount more than 6 times greater than methane). In our experiment the major product is methane: its amount is higher than that which would correspond to the hydrogen balance of the reaction (Eq. (*A*)). Furthermore, the difference in hydrogen balance is even greater than in the previous experiments without silver. Perhaps, the excess hydrogen was abstracted from water adsorbed on the silver coated surface of the glass tube.

Photodissociation of methyl iodide by uv radiation yields, along with hydrocarbons, methylene iodide (in which even one third of all the iodine can be incorporated[32]) and iodoform[9]. No such products were disclosed in the reaction mixture after the methyl iodide decomposition initiated by the CO_2 laser irradiation in the presence of SF_6 (all the iodine was liberated in its elementary form). A relatively high reactivity of organic iodine–containing compounds in the laser experiment can serve as a reason for it. It is known that the $CH_3^{\cdot}$ radical can abstract hydrogen from methylene iodide[9] as much as 16 times faster than from methyl iodide.

Decomposition Performed with Photons Differing in Energy

The decomposition of organic compounds initiated by the CO_2 laser radiation in the presence of SF_6 is generally considered to be a purely thermal process[24]. Surprisingly enough, the reaction course and even the composition of the reaction products was found to be dependent on the wavenumber of exciting line selected from the laser radiation by a grating. We feel that the most acceptable explanation of this phenomenon can be based on the estimation of the absorption cross-section of the individual CO_2 laser lines by SF_6 molecules.

Our experiments have shown that no CH_3I decomposition occurs when the $P(14)$ (948·48 cm^{-1}) and $P(16)$ (947·74 cm^{-1}) lines were used for the irradiation. However, this radiation is not absorbed by SF_6 at all. With the $P(20)$ (944·20 cm^{-1}) line (Table I, exp. 7) the decomposition proceeds; nevertheless only 40% of methyl iodide has been decomposed after 300 s and the reaction mixture contains (considering exps. 7–9 of Table I) the least amount of methane (60%), a large amount of ethane (17%), and no acetylene. On the contrary, the irradiation by the $P(40)$ line (924·98 cm^{-1}) results (Table I, exp. 9), under the same conditions, in 90% conversion and a high yield (80%) of methane and comparatively the highest yield of acetylene (4%). Because no radiation was transmitted through the absorption cell filled with CH_3I/SF_6 mixture, different reaction zones are operative as far as the size and temperature are concerned, as a consequence of a difference between the absorptivity of SF_6 for the individual lines in experiments 7–9. In connection with that we feel that a more detailed examination of properties and the absorption ability of SF_6 is needed. The greatest absorption cross-section is known to be located in the region of wavenumbers somewhat smaller than that of the absorption curve maximum[33] of SF_6. This might be related to the excitation of already excited molecules (hot transitions). The possibility of the effective energy transmission of vibrationally excited SF_6 molecules to, *e.g.*, CH_3I proximate levels can, of course, be also suggested, however, it demands a further study.

Pyrolysis of the CH_3I/SF_6 *Mixture*

As for the pyrolysis of methyl iodide, a study of its rate[12,34] (and the rate changes) have arrested attention more frequently than the analysis of arising products. The question of the decomposition products was, however, scrutinized in a work devoted to the spectroscopy of the methyl radical[14] generated by the pyrolysis of CH_3I. Upon heating to 1200–1400°C methyl iodide affords, besides of methyl radical, methane, ethane and ethylene; analogous perdeuterated products were formed from CD_3I. Thus neither the pyrolysis performed at high temperature leads to the formation of acetylene in such a great amount as that one characteristic for the CH_3I decomposition by laser radiation in the presence of SF_6.

In view of the thermal mechanism of the CH_3I decomposition it was interesting to get in this work an idea of the pyrolysis of the CH_3I/SF_6 mixture. The mixture containing both components in the 5 : 1 ratio was pyrolysed in the arrangement described in the experimental part at three different temperatures. No decomposition proceeded at 450°C. When the mixture was exposed to 660°C and 780°C, the decomposition occurred. Having not knowledge of the conversion but only of the relative amounts of the hydrocarbons in the pyrolytic product mixture, we can state that the main component is methane (660°C–95%, 780°C–90%). In none of the experiments ethane was formed. Ethylene was found in an amount approaching 5%, the rest was represented by acetylene whose content increases with the pyrolysis temperature (660°C – 1%, 780°C – 6%).

REFERENCES

1. Dyubko S. F., Svich V. A., Fesenko L. D.: Opt. Spektrosk. *37*, 208 (1074).
2. Kasper J. V. V., Parker J. H., Pimentel G. C.: J. Chem. Phys. *43*, 1827 (1965).
3. Langsam Y., Lee S. M., Ronn A. M.: Chem. Phys. Lett. *14*, 375 (1976).
4. Robinson J. W., Hailey D. M., Barnes H. M.: Talanta *16*, 1109 (1969).
5. Hamill W. H., Schuler R. H.: J. Amer. Chem. Soc. *73*, 3466 (1951).
6. Schulz R. D., Taylor H. A.: J. Chem. Phys. *18*, 194 (1950).
7. Hudson F. P., Williams R. R., Hamill W. H.: J. Chem. Phys. *21*, 1894 (1953).
8. Schuler R. H., Chmiel C. T.: J. Amer. Chem. Soc. *75*, 3792 (1953).
9. Harris G. M., Willard J. E.: J. Amer. Chem. Soc. *76*, 4678 (1954).
10. Soufie R. D., Williams R. R., Hamill W. H.: J. Amer. Chem. Soc. *78*, 917 (1956).
11. Benson S. W.: J. Chem. Phys. *38*, 1945 (1963).
12. Benson S. W., Spokes G. N.: J. Amer. Chem. Soc. *89*, 2525 (1967).
13. Szwarc M.: Chem. Rev. *47*, 75 (1950).

14. Snelson A.: J. Phys. Chem. *74*, 537 (1970).
15. Petry R. C., Schuler R. H.: J. Amer. Chem. Soc. *75*, 3796 (1953).
16. Donovan J. M., Hanrahan R. J.: Int. J. Radiat. Phys. Chem. *3*, 491 (1971).
17. Kikuch M., Church L. B.: Radiochim. Acta *19*, 128 (1973).
18. Mains J.: U.S. Govt. Res. Develop. Rept. *41*, 56 (1966). Chem. Abstr. *67*, 2587d (1967).
19. Morino Y., Nakamura J.: Bull. Chem. Soc. Jap. *38*, 443 (1964).
20. Engst P., Pola J., Horák M.: This Journal *44*, 406 (1979).
21. McDowell R. S., Galbraith H. W., Krohn B. J., Cantrell C. D.: Opt. Commun. *18*, 64 (1976).
22. Pola J., Engst P., Horák M.: This Journal *44*, 2092 (1979).
23. Cunningham J., Perry A. L.: J. Phys. Chem. *76*, 2353 (1972).
24. Shaub K. M., Bauer S. H.: Int. J. Chem. Kinet. *7*, 509 (1975).
25. Polissar M. J.: J. Amer. Chem. Soc. *52*, 956 (1930).
26. Tsao C. K., Root J. W.: J. Phys. Chem. *76*, 308 (1972).
27. Gose T. A.: J. Amer. Chem. Soc. *82*, 3816 (1960).
28. Rowland F. S., Chan C. C., Angelberger P.: J. Phys. Chem. *75*, 2536 (1971).
29. Reed R. I., Snedden W.: Trans. Faraday Soc. *55*, 876 (1959).
30. Engst P., Pola J., Horák M.: Unpublished results.
31. Donovan R. J., Hathorn F. G. M., Hussain D.: Trans. Faraday Soc. *64*, 3192 (1968).
32. West W., Schlessinger L.: J. Amer. Chem. Soc. *60*, 961 (1938).
33. Brunet H.: J. Quant. Electron. *6*, 678 (1970).
34. Butler E. T., Polanyi M.: Trans. Faraday Soc. *39*, 19 (1943).

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