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Surface reaction of organic materials by laser ablation of matrix-isolated photoreactive aromatic azido compound

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Abstract

The ablation of pentafluorophenylazide (FPA), which was isolated in a chemically inert C_6F_{14} solid matrix at 85 K, was carried out by irradiation with a KrF excimer laser in vacuum. A large amount of pentafluorophenylnitrene (FPN) was ejected explosively as fragments from the matrix during irradiation. The photolysis of FPA was followed by mass spectrometry, UV–visible absorption spectroscopy and optical emission spectroscopy. It was found that the fragment beam of photolysed FPA was useful for the surface chemical modification of organic materials, such as a poly(ethylene terephthalate) film and alkylthiol monolayer. Surface analyses of these materials by X-ray photoelectron spectroscopy and Fourier transform IR reflection absorption spectroscopy indicated that FPN was immobilized on the surface through chemical bonding. The modified surface showed hydrophobic properties due to a decrease in surface polarity by the deposition of the fluorinated group of FPN. © 1997 Elsevier Science S.A.

Keywords: Cryogenic matrix; Excimer laser ablation; Pentafluorophenylazide; Polymer film; Reactive intermediate; Surface reaction

1. Introduction

The ablative photodecomposition of organic materials by excimer lasers is useful for etching, surface modification and thin film deposition [1–4]. The fragments ejected explosively from the surface of materials during ablation include a large number of reactive intermediates, such as radicals and ions [5–9]. On the basis of these studies, it is expected that the reaction of intermediates with polymers may lead to novel chemical modification of polymer surfaces [10], since this method produces a pulsed beam of intermediates with a higher density than that obtained by the pulsed supersonic technique of photolysed molecules [11]. Previously [12], we investigated the chemical reactivity of the intermediates produced by the ablation of a neat solid film of a photoreactive molecule at a cryogenic temperature. Pentafluorophenylazide (FPA), which was photodissociated to a nitrogen molecule and pentafluorophenylnitrene (FPN) with a high quantum yield [13], was used as the photoreactive molecule. However, photolysis in the neat film often induced a side reaction between the photolysed species and the surrounding molecules. The reaction of FPA and FPN to produce decafluoroazobenzene in the film was observed on laser irradiation at low fluence [12].

In this study, we used a chemically inert matrix for photolysis in order to avoid intermolecular reactions, such as the dimerization of intermediates. Since our cryostat could not reach below 85 K, noble gases (i.e. argon and xenon) did not deposit onto the cold plate in vacuum (10^{-4} Pa), and perfluorohexane (C_6F_{14}) was applied as the inert matrix for this technique. Fluorinated alkanes are chemically inert owing to tight C–F chemical bonding compared with hydrocarbons. In addition, the cryogenic fluoroalkane matrix is expected to suppress intramolecular reactions of the intermediates, since organic media show highly effective dispersion of vibrational excess energy from hot intermediates to cool matrix molecules [14]. The reactive intermediates are expected to be trapped in the inert medium.

The photolysis of FPA in an inert matrix at a cryogenic temperature resulted in the trapping of triplet FPN as the major product [15,16]. In general, the photolysis of phenylazides produces phenylnitrenes as minor products in the matrix because the singlet phenylnitrene is liable to proceed to ring-expansion and ring-contraction reactions to form ketenimine and cyanocyclopentadienyl radical [16,17]. In the case of FPN, however, swift formation of triplet FPN suppresses the side reactions of singlet FPN (Scheme 1), because intersystem crossing to the triplet state is accelerated by the internal heavy atom effect of fluorine. Therefore the photolysis of FPA in a cryogenic matrix is suitable for the formation of intermediates with high purity.

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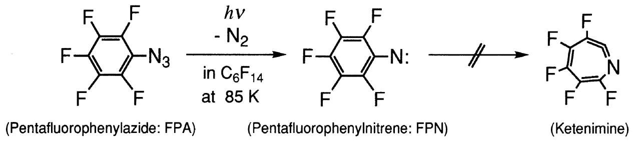

Scheme 1. Photochemical dissociation of pentafluorophenylazide in a cryogenic matrix.

In this study, we monitored the photolysis and ablation of FPA by mass spectrometry, UV–visible absorption spectroscopy and optical emission spectroscopy. The chemical modification of an aromatic polyester film and alkylthiol monolayer was also carried out using a fragment beam from photolysed FPA.

2. Experimental details

The experimental procedure consists of three steps as shown in Fig. 1. First, for the preparation of the solid film of FPA (molecular weight, 209 amu) and C_6F_{14} (PCR Inc., 338 amu), a vapour mixture (deposition ratio, $C_6F_{14} \gg$ FPA) was physically deposited on a sapphire or silver plate at a temperature of 85 K in a vacuum chamber (10^{-4} Pa). The deposition onto the sapphire plate was monitored by transmission absorption spectroscopy with a UV–visible spectrophotometer (Shimadzu, UV-2100). The thickness of the matrix film was set at less than several micrometres. FPA was synthesized from pentafluorophenylhydrazine (Tokyo Chemical Industry Inc.) and sodium nitrite (Nakarai Chemicals, Ltd.) [18].

Second, the deposited film was irradiated with a KrF excimer laser at a wavelength of 248 nm (Lambda Physik, EMG201ESC; FWHM, approximately 20 ns), so that FPA was photolysed on the plate (FPA shows a strong absorption, whereas C_6F_{14} exhibits a negligibly small absorption at 248 nm). A single shot laser irradiation at 100 mJ cm^{-2} $pulse^{-1}$ removed the deposited matrix completely from the substrate during ablation. The fragments ejected explosively from the film were monitored with a quadrupole mass spectrometer (QMS; MKS Instruments Inc., PPT-300EM) using electron impact ionization (impact energy, 75 eV). The optical emission from the surface of the matrix film was collected with a glass fibre and analysed with a solid state polychromator (Hamamatsu, PMA-10). The emission spectrum was accumulated on a computer during laser irradiation at 10 Hz for 10 s.

Finally, a poly(ethylene terephthalate) (PET) film and an alkylthiol monolayer at room temperature were exposed to the fragment beam at a distance of approximately 3 cm from the cryogenic target. The alkylthiol monolayer was fabricated by the dipping of a gold-coated glass plate into an ethanol solution of octadecylthiol (Aldrich) for several hours. The deposit on these substrates was analysed by X-ray photoelectron spectroscopy (XPS; Perkin Elmer Co., PHI-5600ci; X-ray, monochromatic Al Kα) and secondary ion mass spectrometry (SIMS; PHI-5600ci; ion source, Xe^+ ion (4 keV)). The atomic ratio of the polymer surface was estimated from the peak areas of the X-ray photoelectron spectra recorded by fine scanning. Fourier transform IR reflection absorption spectroscopy (IRAS: incident angle, 80°) was also used for the analysis of the alkylthiol monolayer. The IR spectrometer (Perkin Elmer, System 2000 FT-IR) was purged with nitrogen gas to minimize the amount of water vapour and carbon dioxide in the sample chamber.

3. Results and discussion

3.1. Photolysis of FPA in a cryogenic fluorocarbon matrix

When a solid film of FPA and C_6F_{14} on a sapphire or silver plate at 85 K is irradiated with a KrF excimer laser at a fluence of 10 mJ cm^{-2} $pulse^{-1}$, molecular nitrogen (28 amu) is detected by the QMS (Fig. 2). Only nitrogen ejection is synchronized with the pulsed laser radiation in the mass range 1–300 amu. In the UV–visible region, new absorption bands appear on irradiation, as shown in Fig. 3. These spectral changes correspond to the formation of FPN in the triplet state [19]. In addition, the UV–visible spectra show three isosbestic points, suggesting that laser irradiation of FPA in the matrix gives a nitrogen molecule and FPN quantitatively. It was confirmed by UV–visible spectroscopy that FPN in the matrix does not react with C_6F_{14} at 85 K for several hours.

Optical emission spectroscopy is useful for the detection of the byproducts of photolysis because FPN has a large Stokes shift in the visible region. An orange-coloured bright emission is observed from the matrix film after subsequent irradiation (following single shot irradiation) at a fluence in the range 2–50 mJ cm^{-2} $pulse^{-1}$ (Fig. 4). This optical emission spectrum is identical with that of triplet FPN [19]; the emission of FPN can be clearly distinguished from that of pentafluoroketenimine having a peak at approximately 400

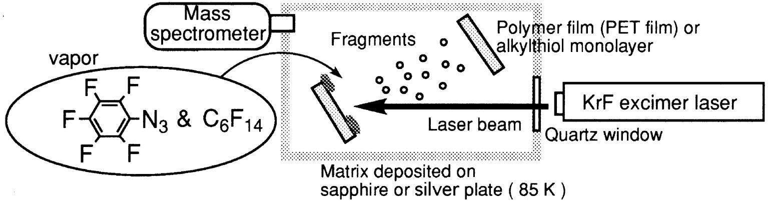

Fig. 1. Schematic drawing of the surface chemical modification of a polymer film using fragments produced by laser ablation of photoreactive molecules in a cryogenic matrix.

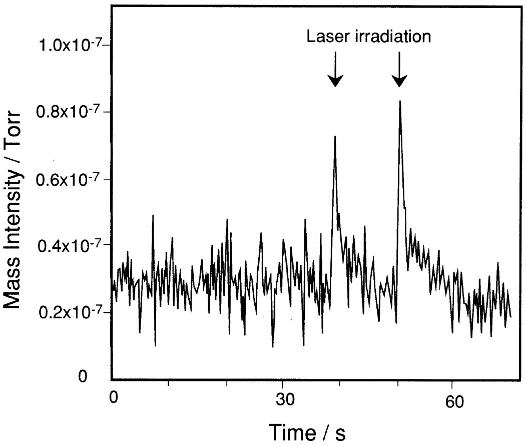

Fig. 2. Mass intensity of molecular nitrogen (28 amu) analysed with a mass spectrometer during KrF excimer laser irradiation of a solid film of FPA and C_6F_{14} on a silver plate at 85 K (fluence, 10 mJ cm^{-2} $pulse^{-1}$).

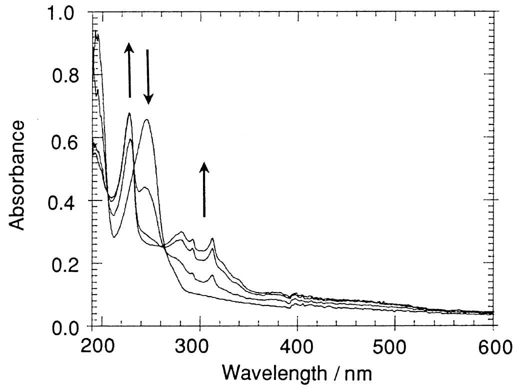

Fig. 3. UV–visible spectral changes of FPA in a C_6F_{14} matrix on a sapphire plate at 85 K on KrF laser irradiation at 2 mJ cm^{-2} $pulse^{-1}$ with 0, 10, 30 and 70 shots. A small peak at 390 nm appears with changing light source.

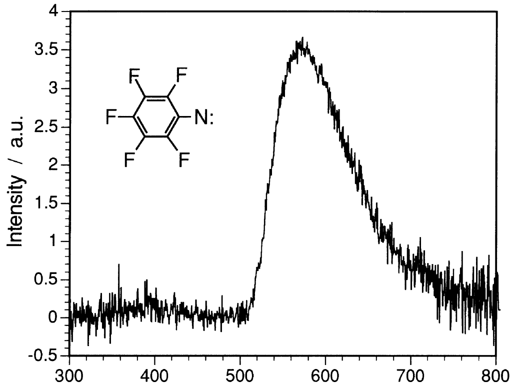

Fig. 4. Optical emission spectrum of FPN in a cryogenic C_6F_{14} matrix at 85 K after photolysis of FPA by KrF laser irradiation at 10 mJ cm^{-2} $pulse^{-1}$. The spectrum was obtained by accumulation of emission on irradiation at 10 Hz for 10 s.

nm [20]. However, when KrF laser irradiation of a neat FPA film without a C_6F_{14} matrix is carried out at 85 K at a fluence of 2 mJ cm^{-2} $pulse^{-1}$, the orange-coloured emission is not observed, mainly because of the dimerization of FPN and FPA [12]. These results indicate that the cryogenic perfluoroalkane matrix is an effective medium for conserving the reactive intermediate.

The ablation threshold of the cryogenic matrix is dependent on the concentration of the dopant and the absorbance of the plates at the laser line (on laser irradiation at 100 mJ cm^{-2} $pulse^{-1}$, a pure C_6F_{14} film on a sapphire plate exhibits no change, whereas a pure film on a silver plate is desorbed explosively by irradiation because the silver absorbs the laser beam at 248 nm). On laser irradiation at a fluence of 100 mJ cm^{-2} $pulse^{-1}$, ablation of the cryogenic solid film results in the explosive ejection of a considerable amount of deposited material from the plates (although $C_3F_5^+$ (131 amu), CF_3^+ (69), CF^+ (31) and N_2^+ (28) are detected by the QMS, FPN^+ (181) and FPA^+ (209) are not detected, probably because the concentration of FPA in the matrix is lower than that of C_6F_{14}). Although the threshold for the neat film of FPA is approximately 25 mJ cm^{-2} $pulse^{-1}$ for KrF excimer laser irradiation [12], the threshold of the mixed matrix film is estimated to be between 50 and 100 mJ cm^{-2} $pulse^{-1}$. For irradiation at 50 mJ cm^{-2} $pulse^{-1}$, the results of mass, absorption and emission analyses are similar to those of FPA photolysis induced by low fluence irradiation, so that the multiphoton reaction of FPA will not be dominant for irradiation at 100 mJ cm^{-2} $pulse^{-1}$. The ablation of the cryogenic matrix film involves both photochemical and photothermal mechanisms, because the fluorocarbon molecules are physically desorbed from the plate above approximately 180 K in the vacuum chamber.

3.2. Surface modification of organic thin film using the fragments of ablated azide

The chemical reactions on a PET film, induced by the reactive intermediates produced in the ablation, were studied by investigating the surface modification of the film. After treatment with the fragments produced on KrF laser irradiation at 100 mJ cm^{-2} $pulse^{-1}$ (three shots), new F_{1s} and N_{1s} peaks are observed in the X-ray photoelectron spectrum of the PET film (Fig. 5), indicating that the reactive intermediates produced by the ablation of the matrix film are immobilized through chemical bonding on the PET surface. The chemical modification is also confirmed by SIMS for negative ions; new peaks at mass numbers of 19 amu (F^- ion) and 26 amu (CN^- ion) are detected on the treated PET film.

The C_{1s} peaks in fine XPS scanning include a new peak whose position appears at a higher binding energy compared with those of the original PET film because of the immobilization of the fluorocarbon species on the surface. The chemical reactivity of the fragments with the polymer is mainly attributed to nitrene and not to C_6F_{14}, because the treated surface shows a six times higher atomic ratio of fluorine compared with that of nitrogen (Table 1). These results indicate that most of the C_6F_{14} molecules ejected explosively from the plate show no chemical reactivity with the surface, and that the ablation of the cryogenic matrix produces a reactive molecular beam with a high density pulse.

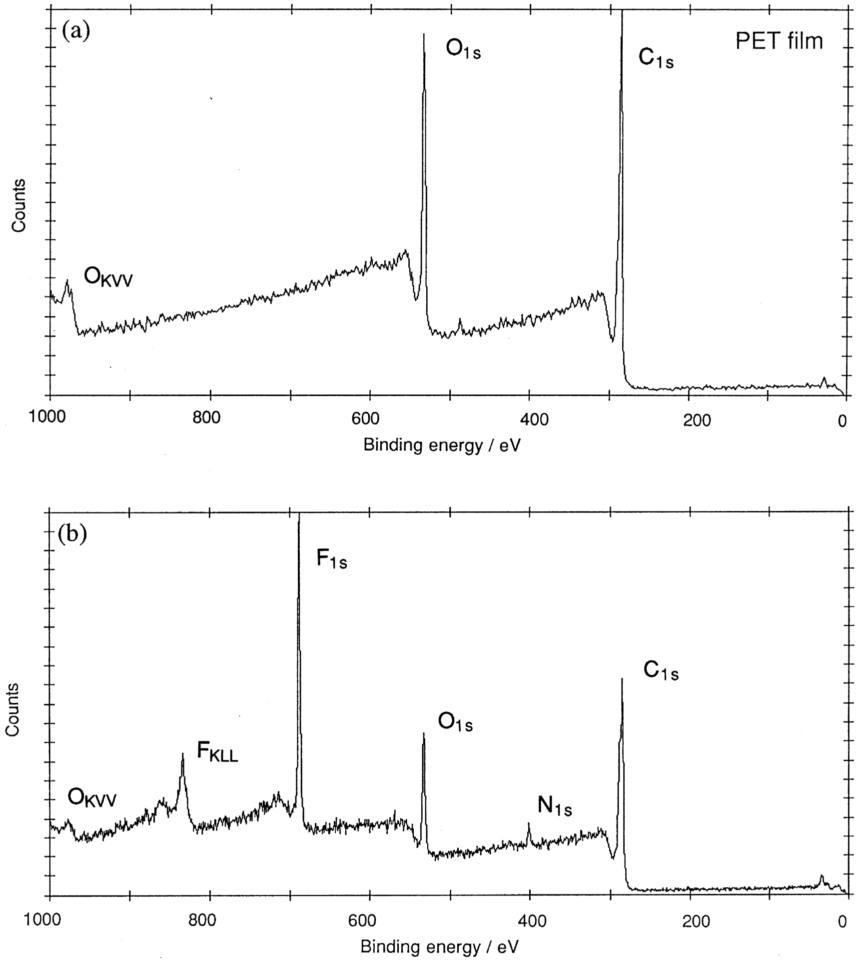

Fig. 5. X-Ray photoelectron spectra recorded with a survey scan from the surface of the PET film: before (a) and after (b) laser treatment (KrF laser, 100 mJ cm^{-2} pulse^{-1}, three shots).

Table 1
Atomic ratio of PET surface before and after treatment using fragments generated by KrF laser ablation of pentafluorophenylazide in a C_6F_{14} matrix at 85 K [a]

	Carbon	Oxygen	Nitrogen	Fluorine
Before laser treatment	10	3.4	– [b]	– [b]
After laser treatment (100 mJ cm^{-2} pulse^{-1}, three shots)	10	2.0	0.5	3.2

[a] Atomic ratio was estimated by calculation of the peak areas in high-resolution X-ray photoelectron spectra recorded with fine scanning (atomic factor: $C_{1s}:N_{1s}:O_{1s}:F_{1s}=0.296:0.477:0.711:1.000$).
[b] Not detected.

This interpretation is supported by IRAS measurements of an alkylthiol monolayer. Fig. 6 shows the IR reflection absorption spectra before and after laser treatment of an octadecylthiol monolayer on a gold film. Although both spectra in Fig. 6(a) and Fig. 6(b) show the C–H vibrations of the alkyl group at 2800–3000 cm^{-1}, a new peak appears at 1522 cm^{-1} after laser treatment (Fig. 6(b)). This peak can be ascribed to the C–C stretching vibration of the aromatic ring on FPN in comparison with that of FPA, indicating that FPN is immobilized on the surface without structural changes such as ring expansion. However, when a neat film of FPA is used for this modification, an additional peak at 1730 cm^{-1}, ascribed to the stretching vibration of carbonyl groups, is observed on the monolayer after laser treatment. The carbonyl groups will be produced by the reaction of a dangling bond on the modified surface with ambient oxygen when the sample is taken out of the chamber for IRAS measurement. These phenomena show that a selective and mild reaction occurs using the matrix method.

On the basis of the above-mentioned results of FPN immobilization, the contact angle of the surface was studied from the viewpoint of the surface polarity. The contact angle of the alkylthiol surface with water changes from 90° to 130° by laser treatment (three shots). The hydrophobic change can be explained by fluorocarbon deposition on the surface. Although the surface modification of polyacetylene with a

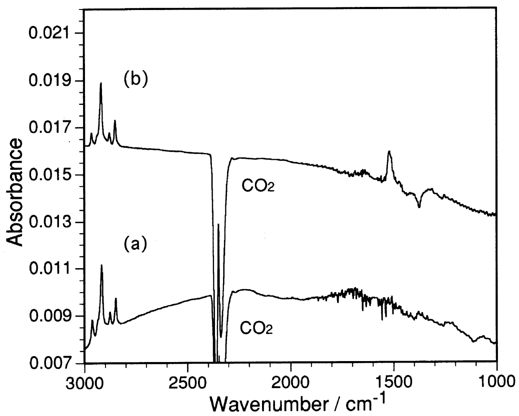

Fig. 6. IR reflection absorption spectra of a monolayer of octadecylthiol on a gold film: before (a) and after (b) laser treatment (KrF laser, 100 mJ cm^{-2} $pulse^{-1}$, 1 shot).

pulsed supersonic beam is detected after exposure to more than 10^4 shots of a photolysed HN_3 beam [11], our method requires only several shots for surface modification.

Our ablation mechanism is clearly distinct from matrix-assisted laser desorption ionization (MALDI), which is applied to the mass analysis of synthetic polymers, proteins and DNA having a huge molecular weight [21]. Although MALDI uses matrix molecules with high absorption at the laser excitation wavelength, our host molecule in the matrix is chemically inert and exhibits a negligibly small absorption at the laser excitation wavelength; therefore our cryogenic matrix provides a suitable environment for reactive intermediate formation by laser photolysis. These intermediates retain their chemical reactivity when they are ejected into a gaseous atmosphere. Moreover, a wide variety of reactive fragments are produced by experimentally controlled ablation, and many kinds of polymer film can be chemically modified by our method.

4. Conclusions

A new technique for chemical surface modification of organic materials, such as aromatic polyesters and alkylthiol monolayers, is offered by the laser ablation of photoreactive monomeric molecules in a chemically inert matrix at cryogenic temperatures. In our technique, several shots of fragment exposure are sufficient for detectable modifications, because excimer laser ablation produces a pulsed beam of reactive fragments with a higher density.

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References

[1] D. Bäuerle, Laser Processing and Chemistry, Springer, Berlin, 2nd Ed., 1996, p. 191.
[2] R. Srinivasan, B. Braren, Chem. Rev. 89 (1989) 1303.
[3] M. Ouyang, H. Hiraoka, Appl. Phys. Lett. 67 (1995) 1781.
[4] S. Lazare, R. Srinivasan, J. Phys. Chem. 90 (1986) 2124.
[5] H. Sato, Res. Chem. Intermed. 19 (1993) 67.
[6] Y. Tsuboi, K. Hatanaka, H. Fukumura, H. Masuhara, J. Phys. Chem. 98 (1994) 11 238.
[7] Y. Tsuboi, H. Fukumura, H. Masuhara, J. Phys. Chem. 99 (1995) 10 305.
[8] M. Kobayashi, A. Sato, Y. Tanaka, H. Shinohara, H. Sato, Appl. Organomet. Chem. 7 (1993) 303.
[9] H. Niino, A. Yabe, Appl. Surf. Sci. 69 (1993) 1.
[10] H. Niino, A. Yabe, Chem. Lett. (1994) 1223.
[11] D.C. Weber, A.P. Baronavski, T.P. Heavner, C.L. Gordon III, J. Chem. Soc., Chem. Commun. (1987) 912.
[12] H. Niino, A. Yabe, Appl. Surf. Sci. 96–98 (1996) 572.
[13] C.H. Lee Go, W.H. Waddell, J. Am. Chem. Soc. 106 (1984) 715.
[14] B.F. LeBlanc, R.S. Sheridan, J. Am. Chem. Soc. 110 (1988) 7250.
[15] I.R. Dunkin, P.C.P. Thomson, J. Chem. Soc., Chem. Commun. (1982) 1192.
[16] A. Marcinek, M.S. Platz, S.Y. Chan, R. Floresca, K. Rajagopalan, M. Golinski, D. Watt, J. Phys. Chem. 98 (1994) 412.
[17] D.W. Cullin, N. Soudararajan, M.S. Platz, T.A. Miller, J. Phys. Chem. 94 (1990) 8890.
[18] J.M. Birchall, R.N. Haszeldine, A.R. Parkinson, J. Chem. Soc. (1962) 4966.
[19] E. Leyva, M.S. Platz, G. Persy, J. Wirz, J. Am. Chem. Soc. 108 (1986) 3783.
[20] R. Poe, K. Schnapp, M.J.T. Young, J. Grayzar, M.S. Platz, J. Am. Chem. Soc. 114 (1992) 5054.
[21] M. Karas, F. Hillenkamp, Anal. Chem. 60 (1988) 2299.