

## Surface Photochemistry: Evidence for Rotational and Translational Movement of Cyanopropyl Radicals on a Silica Gel Surface

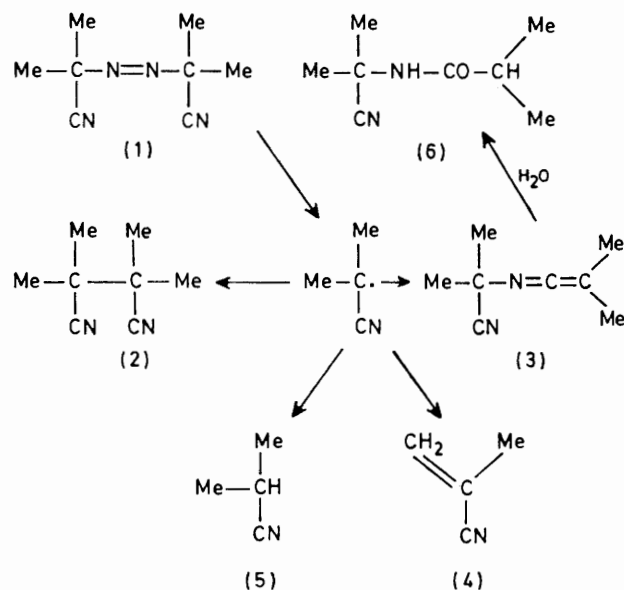
Linda J. Johnston, Paul de Mayo,\* and S. King Wong\*

*Photochemistry Unit, Department of Chemistry, University of Western Ontario, London, Ontario N6A 5B7, Canada*

The photolysis of azoisobutyronitrile is shown to generate radicals which, contrary to an earlier report, undergo rotational and translational movement on a silica gel surface.

Hitherto little evidence has been provided with respect to the possibilities of rotational and translational movement of radicals and, in particular, radical pairs on a surface. Recently, limited translational motion has been shown to occur on dry silica gel, and to precede recombination in a singlet radical pair generated in the photo-Fries rearrangement.<sup>1</sup> A greater

degree of translational movement was observed when a singlet or triplet radical pair was generated on silica gel by photolysis of a benzyl phenylacetate or a dibenzyl ketone, respectively.<sup>2</sup> Similar results have also been reported for radical pairs generated on silica gel from azocumene<sup>3a</sup> and diacyl peroxides,<sup>3b</sup> although decomposition of the latter is apparently



Scheme 1

complicated by the intervention of ionic processes. In sharp contrast, the photolysis of azoisobutyronitrile (AIBN) (1) in a silica gel-benzene matrix has been reported to lead to the formation of (2) only, with the claim that the cyanopropyl radicals generated were not free to rotate, and so did not produce the alternative, unsymmetrical, coupling product (3) as occurs in solution.<sup>4</sup> This claim appears to have been generally accepted.<sup>5</sup> We have reinvestigated this system and report results which require revision of this view and which, in addition, demonstrate that cyanopropyl radicals on silica gel undergo translational movement.

The solution thermolysis<sup>6</sup> and photolysis<sup>7</sup> of AIBN have been studied extensively. The loss of nitrogen (Scheme 1) produces two radicals which couple to produce both (2) and (3) (benzene, yields 60% and 30%, respectively, by thermolysis and 40% and 55%, respectively, by photolysis), and disproportionate to give (4) and (5) (ca. 5% yield by both thermolysis and photolysis). On the other hand, McBride<sup>8a</sup> has found that in the solid state photolysis 80–90% of the products arises from disproportionation. Leermakers<sup>4</sup> observed spectroscopically the disappearance of (1) in a silica gel-benzene slurry on irradiation, but did not observe the formation of (3); a 90% yield of (2) (isolated) was reported for a large scale irradiation.

To test for the stability of (3), and the possibility that it might be converted into (2), silica gel was added to a 1 mm cuvette containing 0.113 M (3) in benzene. The slurry showed a gradual decrease in the absorption at 290 nm (ca. 50% decrease after 50 min). From preparative experiments the decrease in absorption was shown to be entirely attributable to the formation of *N*-(1-cyano-1-methylethyl)isobutyramide, (6).<sup>8</sup> There was  $\geq 30\%$  hydrolysis of (3), even for silica gel which had been dried at 200 °C *in vacuo* before use.

Irradiation of AIBN in a silica gel-benzene slurry gave substantial amounts of (3) and the amide (6) derived from it (Table 1). In general, the sum of (3) and (6) represents ca. 50% of the isolated products. This result is similar to that found for photolysis in solution and indicates clearly that there is little restriction on the rotation of the cyanopropyl radicals. The results in Table 1 show that the incompatibility of our results with the earlier report<sup>4</sup> cannot be attributed to light intensity,

Table 1. Photolysis of AIBN in silica gel-benzene slurries and on dry silica gel.

| Conditions <sup>a</sup>               | Temperature/<br>°C | Product distribution/% <sup>b</sup> |     |     |
|---------------------------------------|--------------------|-------------------------------------|-----|-----|
|                                       |                    | (2)                                 | (3) | (6) |
| Slurry <sup>c</sup> , A, C            | 20                 | 43                                  | 16  | 41  |
| Slurry, A, C                          | 20                 | 48                                  | 13  | 38  |
| Slurry, A, C                          | 40 <sup>e</sup>    | 57                                  | 2   | 43  |
| Slurry, A, D                          | 20                 | 50                                  | 13  | 37  |
| Slurry, B, C                          | 20                 | 55                                  | 14  | 30  |
| Slurry, B, C                          | 52 <sup>e</sup>    | 58                                  | —   | 52  |
| Slurry, B, D                          | 20                 | 59                                  | 34  | 7   |
| Slurry, A, F, D                       | 10                 | 62                                  | —   | 38  |
| Slurry, A, F, E                       | 10                 | 66                                  | —   | 33  |
| Dry silica gel (G), <sup>d</sup> A, C | 10                 | 53                                  | 16  | 31  |
| Dry silica gel (G), A, C              | 10                 | 58                                  | 13  | 29  |
| Dry silica gel (H), A, C              | 10                 | 63                                  | 25  | 12  |
| Dry silica gel (H), A, C              | 10                 | 73                                  | 9   | 17  |

<sup>a</sup> Merck silica gel 60 (35–70 mesh) was used as received; A, medium pressure Hanovia Hg lamp; B, high pressure Hg lamp, shorter irradiation time; C, Corning 7-60 filter ( $\lambda > 330$  nm); D, Pyrex; E, quartz; F, immersion well. <sup>b</sup> Determined by <sup>1</sup>H n.m.r. integration (internal standard) at 60–95% conversion. <sup>c</sup> Slurry sample concentrations were 0.281 mmol AIBN/g silica gel/2.0 ml benzene; samples were not degassed. <sup>d</sup> Dry silica gel samples were degassed to 10<sup>-5</sup> Torr; coverages were 0.403 mmol AIBN/g silica gel (G) and 0.0812 mmol/g (H). <sup>e</sup> 5% Dark decomposition of AIBN to (2) occurred under these conditions.

or to temperature variations, or to the use of Pyrex instead of a 330 nm cut-off filter, since these have little effect on the product ratios [except for variations in the amount of hydrolysis of (3)]. Two large scale photolyses of AIBN in a silica gel-benzene matrix in an immersion well, using either a quartz or Pyrex filter, both yielded substantial amounts of amide (6). Finally, a slurry of (3) irradiated through Pyrex yielded 27% amide (6) and 70% (3), with no other products detected by <sup>1</sup>H n.m.r. spectroscopy. We conclude that the earlier observation<sup>4</sup> is in error.

Samples of AIBN adsorbed on dry silica gel at two coverages were irradiated.† The product distribution (Table 1) was qualitatively similar to that obtained in the slurry experiments; again, some hydrolysis of (3) was observed. In these experiments the isolation procedure could have resulted in loss of volatile compounds such as (4) and (5). A search for these from irradiation of AIBN on dry silica gel at 25% coverage showed the presence of ca. 5% (5).

The formation of (3) on dry silica gel also requires that rotation of the cyanopropyl radicals should occur. Evidence for translational movement was then sought. Photolysis of mixtures of [<sup>2</sup>H<sub>0</sub>]AIBN and [<sup>2</sup>H<sub>12</sub>]AIBN and deuterium content analysis of the recovered amide (6)‡ showed that significant amounts of [<sup>2</sup>H<sub>6</sub>]amide were formed.§ The escape of cyanopropyl radicals from the initial geminate pair indicated that translational movement of these radicals also occurred. The similarity of the surface product ratios to those in solution and their difference from results obtained in the crystalline phase provides evidence that the restrictions on rotational and translational motion on the dry silica gel surface are not severe.

† Determined by calculation to be 25% and 5%.

‡ For a typical experiment the ratios of [<sup>2</sup>H<sub>0</sub>]:[<sup>2</sup>H<sub>6</sub>]:[<sup>2</sup>H<sub>12</sub>] were 84.5:17.0:100 for dry silica gel at 25% coverage and 90.9:23.0:100 for a slurry.

§ The results of a detailed study will be published elsewhere.

The authors thank the donors of the Petroleum Research Fund administered by the American Chemical Society and the National Science and Engineering Research Council of Canada for support of this work.

Received, 28th June 1982; Com. 749

### References

- 1 D. Avnir, P. de Mayo, and I. Ono, *J. Chem. Soc., Chem. Commun.*, 1978, 1109.
  - 2 D. Avnir, L. J. Johnston, P. de Mayo, and S. K. Wong, *J. Chem. Soc., Chem. Commun.*, 1981, 958.
  - 3 (a) J. E. Leffler and J. J. Zupancic, *J. Am. Chem. Soc.*, 1980, **102**, 259; (b) J. E. Leffler and J. T. Barbas, *ibid.*, 1981, **103**, 7768.
  - 4 P. A. Leermakers, L. D. Weis, and H. T. Thomas, *J. Am. Chem. Soc.*, 1965, **87**, 4403; P. A. Leermakers, H. T. Thomas, L. D. Weis, and F. C. James, *ibid.*, 1966, **88**, 5075.
  - 5 See, for instance, (a) A. B. Jaffe, K. J. Skinner, and J. M. McBride, *J. Am. Chem. Soc.*, 1972, **94**, 8510; (b) H. Werbin and E. T. Strom, *ibid.*, 1968, **90**, 7296; (c) L. Ebersson, *Electrochim. Acta*, 1967, **12**, 1473.
  - 6 M. Talat-Erben and S. Bywater, *J. Am. Chem. Soc.*, 1955, **77**, 3710, 3712, and references therein.
  - 7 P. Smith and A. M. Rosenberg, *J. Am. Chem. Soc.*, 1959, **81**, 2037, and references therein.
  - 8 R. M. Haines and W. A. Waters, *J. Chem. Soc.*, 1958, 3221.
-