New methods in chemical actinometry

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The use of the well-known iron oxalate solution (Parker) causes various problems: (a) during the whole of the irradiation time total absorption must be guaranteed; (b) red light is necessary during the tedious analytical procedure, which must be precise; (c) the photoproducts absorb at certain wavelengths and therefore the degradation yield has to be less than 5%; (d) the proposed correction factor cannot be recommended at wavelengths longer than 450 nm; (e) recently, diverse restrictions have been published; (f) the results cannot be standardized for the actinometry of lasers. For these reasons the *trans–cis* photoisomerization of azobenzene was examined and proved to be a convenient actinometer between 254 and 436 nm and for intensity measurements of a nitrogen laser (337.1 nm). Each experiment gave many independent intensity values for the light source by use of a specific photokinetic measurement and evaluation method. Another new photochromic system for wavelengths between 300 and 600 nm is discussed.

Photochemical determination of the high pressure limiting rate constant of the reaction H + NO + M = HNO + M

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The reaction H + NO + M = HNO + M was investigated as a function of inert gas pressure (M ≡ N_2, Ar) from 0.5 to 1200 atm at 303 and 313 K, using steady state quasi-monochromatic ($\lambda = 250 \pm 20$ nm) photolysis of a mixture of NO and HI. The evolution of the steady state was followed spectrophotometrically via the disappearance of HI and/or the formation of molecular iodine. The transition pressure was found to be approximately 60 atm and the high pressure limiting rate constant $k_{3,\infty}$ attained at pressures over 400 atm was measured as $\log k_{3,\infty} = 14.7 \pm 0.35$ cm^3 mol^{-1} s^{-1} at 313 K for M ≡ N_2. Using the Cas-

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sel curve method of Troe [1], extrapolation of our measurements with $M \equiv Ar$, made at pressures under 100 atm, yielded the value 1.5×10^{14} cm^3 mol^{-1} s^{-1} for $k_{3,00}$. Both these determinations are at least a factor of 2 higher than the calculations of Quack and Troe [2].
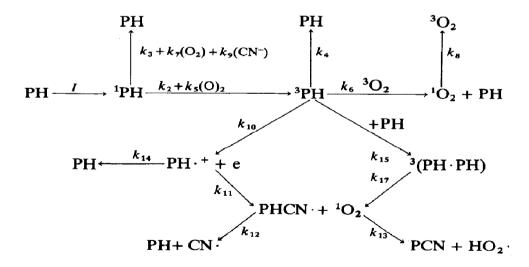
1 J. Troe, *Ber. Bunsenges.*, *78* (1974) 478.
2 Quack and J. Troe, *Ber. Bunsenges. Phys. Chem.*, (1978).

Nucleophilic photocyanation of phenanthrene in anhydrous acetonitrile containing oxygen and 18-crown-6-ether

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The following mechanism is proposed:

Values for the rate constants k_2 - k_8 were found from the literature and values for the rate constants k_9 - k_{17} were calculated from experimental results.