# Flash Photolysis of *N*-Bromo-3,3-dimethylglutarimide: Detection of the Imidyl Radical

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*Summary* A transient, ascribed to an imidyl radical, has been observed in the flash photolysis of *N*-bromo-3,3-dimethylglutarimide in carbon tetrachloride solution; both the transient as well as the precursor were quenched by 3,3-dimethylbut-1-ene while cyclohexane quenched the transient but not the precursor.

UNDER conditions where halogen atom chain processes are suppressed, the decomposition of *N*-halogeno-imides, notably of *N*-bromosuccinimide, generates imidyl radicals as the dominant reactive species.[1-4] Imidyl radicals add to alkenes and aromatic nuclei[4,5] and abstract hydrogen atoms from alkyl groups;[1-6] addition generally occurs preferentially. Studies of the dependence of product distribution on the reaction conditions in the photolysis of *N*-bromosuccinimide and related compounds suggest the presence of two imidyl radical intermediates (attributed to the ground and the lowest excited radical) which exhibit quite different chemical reactivities.[3,6] We here report the direct observation of a reactive intermediate in the flash photolysis of deoxygenated solutions of carefully purified *N*-bromo-3,3-dimethylglutarimide (**1**) in $CCl_4$. Here, the moderate concentrations of (**1**), negligible or low product buildup, and relatively high transient concentrations associated with flash photolysis studies tend to minimize the importance of chain processes and secondary species as compared with continuous irradiation studies requiring the analysis of reaction products.

Freshly prepared argon-deoxygenated $CCl_4$ solutions of (**1**) (0·01 M) were subjected to flash discharges (0·8 $\mu$s, 79 J)[7] at room temperature through a $CCl_4$ filter (cutoff $<260$ nm) for only a few times before being discarded. The extent of $Br_2$ buildup under these photolysis conditions was inferred from separate experiments in which (**1**) was flash photolysed in acetonitrile solution and the buildup of $Br_2$ absorption at 270 nm with number of flashes measured. The concentration of $Br_2$, undetectable before photolysis, increased to *ca.* $7 \times 10^{-7}$ M after several photolysis flashes. When the $CCl_4$ solution of (**1**) was flash photolysed, a transient increasing in absorption from 400 nm to $<345$ nm [the short wavelength limit due to the absorption of (**1**)] decaying by second order kinetics was observed.† No difference in the transient absorption or kinetics was observed over the first few flashes. Photolysis of degassed $CCl_4$ (Fisher spectrograde) solvent alone produced only a weak, broad, background transient absorption between 335 and 400 nm.

When 3,3-dimethylbut-1-ene ($0{\cdot}78 \times 10^{-8}$ M) was added to the solution of (**1**), the transient decayed by first order kinetics with a lifetime of 78 $\mu$s. Upon addition of further butene, both the zero-time transient absorbance and lifetime decreased, until at $11{\cdot}7 \times 10^{-4}$ M $Me_3CCH{=}CH_2$, the zero-time absorbance was reduced to *ca.* 1/3 of the original unquenched value and the lifetime was 43 $\mu$s. The reduction in the transient lifetime with concentration of the butene corresponds to a quenching rate constant of $k_A = 9 \times 10^6$ dm$^3$ mol$^{-1}$ s$^{-1}$. As the butene absorbed an insignificant amount of the filtered photolysis light, quenching of the zero-time absorbance of the signal can be attributed to quenching of the precursor of the transient. The decrease in absorbance of the transient with $Me_3CCH{=}CH_2$ is expressed by a plot of $A_0/A$ *vs.* [$Me_3CCH{=}CH_2$], where $A$ and $A_0$ are the initial transient absorbance with and without the butene, respectively. The data are not sufficiently accurate to establish the linearity of the dependence but

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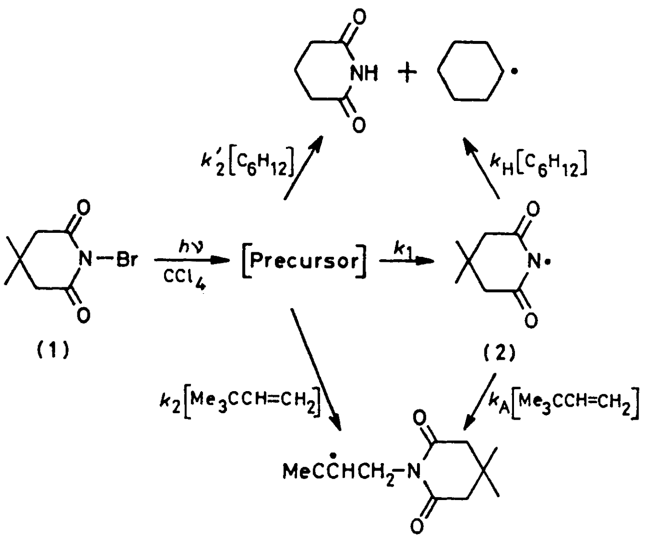
† A second weaker transient ($\lambda_{max}$ 450 nm) was also observed but was not affected by concentrations of up to $4 \times 10^{-3}$ M of $Me_3CCH{=}CH_2$.

do show unequivocally that strong quenching is occurring. A straight-line fit to the data, assuming a Stern–Volmer-type *kinetic* relationship, yields a ratio of $k_2/k_1$ of $1 \times 10^3$ dm$^3$ mol for competition between quenching of the precursor by olefin ($k_2$ [olefin]) and the rate of formation of the transient ($k_1$). Since the transient is formed in less than *ca.* 5 $\mu$s ($k_1 > 2 \times 10^5$ s$^{-1}$) the rate constant for quenching of the precursor by 3,3-dimethylbut-1-ene is $k_2 > 2 \times 10^8$ dm$^3$ mol$^{-1}$ s$^{-1}$.

The transient was also quenched by cyclohexane ($k_H = 3{\cdot}5 \times 10^3$ dm$^3$ mol$^{-1}$ s$^{-1}$), but at concentrations of cyclohexane of $\leqslant 2$ M in $CCl_4$ quenching of the precursor was not observed. The rate of the reaction of the precursor with these concentrations of cyclohexane, $k_2'$[cyclohexane], a source of secondary substituted hydrogens, is evidently not sufficiently high to compete with $k_1$. Hydrogen abstraction by the precursor is therefore nowhere near diffusion controlled. The transient showed even less reactivity towards hexamethylethane, a source of primary hydrogens. At concentrations of hexamethylethane of $\leqslant 0{\cdot}5$ M, quenching of the transient lifetime or absorption was not sufficiently large to be measured reliably.

Although, *a priori*, the transient may be one of several radical species, the experimental result is consistent only with the transient being the imidyl radical (**2**). The $CCl_3$ radical absorbs only below 300 nm ($\lambda_{max} < 230$ nm).[8] Furthermore, the rate of quenching of the transient (**2**) by olefin and alkane is inconsistent with the known reactivity of the $CCl_3$ radical, [9] and no product derived from the $CCl_4$ solvent has been reported or found by us in steady state studies. The flash photolysis of 1-bromoheptane in $CCl_4$ to produce alkyl radicals ($\lambda_{max} < 240$ nm)[10] and Br atoms resulted in a transient absorption which was not affected by $4 \times 10^{-2}$ M $Me_3CCH{=}CH_2$; a concentration *ca.* 20 times higher than that necessary for the complete quenching of the transient (**2**) from the solution of (**1**).



Scheme

The present results clearly show the presence of two consecutive reactive species competing for substrate molecules as shown in the Scheme. The transient imidyl radical (**2**) reacts with substrates by addition or hydrogen abstraction with characteristic rate constants. The precursor presumably reacts in the same manner but its contribution to the overall reaction is determined by the competition of the unimolecular transformation into (**2**) ($k_1$) and the bimolecular reactions with substrates ($k_2$, $k_2'$). In the case of (**1**), it appears that the former, $k_1$, is very fast. The precursor is possibly another electronic state[3,6] of the observed imidyl radical or, alternatively, an excited state of (**1**).

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