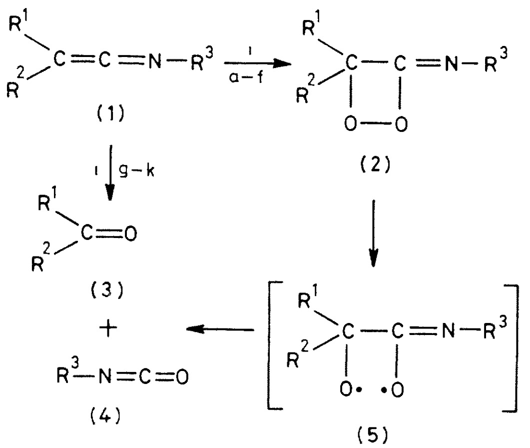
Chemiluminescence of Imino-1,2-dioxetan Formed from Ketenimine and Singlet Oxygen[1]

By YOSHIKATSU ITO,* HIROAKI YOKOYA, KAZUAKI KYONO, SOICHIRO YAMAMURA, YUTAKA YAMADA, and TERUO MATSUURA

(*Department of Synthetic Chemistry, Faculty of Engineering, Kyoto University, Kyoto* 606, *Japan*)

Summary The chemiluminescent properties of several imino-1,2-dioxetans prepared by the photosensitized oxygenation of ketenimines at −78 °C, indicate that the energy level of the transition state for their decomposition to the corresponding ketones and isocyanates is low and that the decomposition proceeds *via* a biradical mechanism

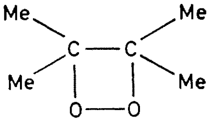
IN contrast to the extensive investigation of the chemiluminescent thermal decomposition of simple dioxetans and dioxetanones,[2] work on the luminescent properties of iminodioxetans has only recently been published, independently, by ourselves and Adam *et al* [3,4] We have reported a one-step approach to the imine (**2a**) by the low temperature photo-oxygenation of the ketenimine (**1a**) [3] The total yield of excited-state products from (**2a**) was dramatically lower than that from the structurally related tetramethyl-1,2-dioxetan (**6**) or dimethyl-1,2-dioxetanone (**7**)[3] and we have investigated further this inefficiency in the formation of the excited state from (**2a**). We report here a number of new iminodioxetans synthesized by the same procedure and the effect of ring-substituents on the luminescent properties of imino dioxetans.

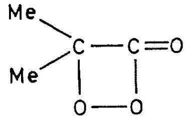


a; $R^1 = R^2 = Me$, $R^3 = Bu^t$
b; $R^1 = R^2 = Et$, $R^3 = Bu^t$
c; $R^1 = R^2 = Et$, $R^3 = Pr^i$
d; $R^1 = R^2 = Me$, $R^3 = C_6H_{11}$
e; $R^1 = Ph$, $R^2 = Me$, $R^3 = Bu^t$
f; $R^1 = Ph$, $R^2 = Bu^n$, $R^3 = Bu^t$
g; $R^1 = R^2 = Me$, $R^3 =$ *p*-tolyl
h; $R^1 = R^2 = Me$, $R^3 =$ α-naphthyl
i; $R^1 = R^2 = Ph$, $R^3 = Bu^t$
j; $R^1 = Ph$, $R^2 = Bu^n$, $R^3 =$ *p*-tolyl
k; $R^1 = R^2 = R^3 = Ph$

SCHEME. i, $^1O_2$, −78 °C.

The imines (**2a**)–(**2f**) were prepared by the previous method[3] in good yields from the ketenimines (**1a**)–(**1f**) and singlet oxygen at −78 °C in $CFCl_3$ or CH_2Cl_2 using tetraphenylporphine (TPP) or polymer-bound Rose Bengal as the sensitizer. As shown in Table 1, these ketenimines readily reacted with singlet oxygen with rates comparable to that of tetramethylethylene. In contrast with the trialkylketenimines (**1a**)–(**1d**) and alkylaryl-*N*-alkylketenimines (**1e**) and (**1f**), the dialkyl-*N*-arylketenimines (**1g**) and (**1h**), alkyldiarylketenimines (**1i**) and (**1j**), and triphenylketenimine (**1k**) produced no detectable iminodioxetans (at −70 °C; ^1H n.m.r.). Only the corresponding ketones (**3**) and isocyanates (**4**) were produced.


(**6**)


(**7**)

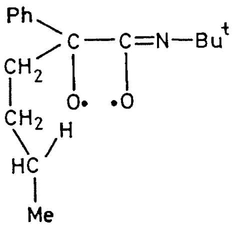

(**8**)

TABLE 1. Photosensitized oxygenation of ketenimines (**1a**)—(**1f**) with singlet oxygen at −78 °C.[a]

Ketenimines	Relative rate[b]	Iminodioxetan (**2**) yield/%[c]
(**1a**)	1·0	65
(**1b**)	2·0	72
(**1c**)	0·56	88
(**1d**)	1·1	50
(**1e**)	0·12	59
(**1f**)	0·10	55

[a] In $CFCl_3$ using TPP as sensitizer. [b] Rate of reaction with singlet oxygen as compared with that of tetramethylethylene (rel. rate, 1·0). Determined by the competition method. [c] Determined by ^1H n.m.r. spectroscopy at −70 °C. Other major products were the corresponding ketones (**3**) and isocyanates (**4**).

The ^1H n.m.r. spectra of the iminodioxetans (**2a**)–(**2f**) are summarized in Table 2. While (**2a**)–(**2f**) were stable at −78 °C for many hours, they decomposed to the corresponding ketones and isocyanates even at −30 °C with the following rate constants (**2a**) 9·6 × 10^{-3}, (**2b**) 9·8 × 10^{-3}, (**2c**) 1·1 × 10^{-3}, (**2d**) 5·9 × 10^{-4}, (**2e**) 5·8 × 10^{-2}, and (**2f**) 4·0 × 10^{-2} s^{-1}, respectively.† Their activation energies ranged from 15 to 18 kcal/mol (1 cal = 4·184 J), *i.e.* (**2a**) 17·6,[3] (**2b**) 16·7, (**2c**) 18·3, (**2d**) 17·5, (**2e**) 15·4, and (**2f**) 15·3 kcal/mol (estimated error ±2 kcal/mol). It can be seen that a phenyl group has a destabilizing effect. Interestingly, (**2f**) afforded a 0·4% yield (by g.l.c.) of acetophenone, a Norrish type II product of valerophenone, in addition to valerophenone and t-butyl isocyanate.

TABLE 2. ^1H N.m.r. spectra of the iminodioxetans (**2a**)—(**2f**).

Iminodioxetan	δ (in $CFCl_3$ at −70 °C)
(**2a**)	1·64 (s, Me) and 1·22 (s, Bu^t)
(**2b**)	1·20 (t, *J* 7 Hz, Et), 1·75 (q *J* 7 Hz, Et), and 1·23 (s, Bu^t)
(**2c**)	1·18 (t, *J* 7 Hz, Et), 1·80 (q, *J* 7 Hz, Et), 1·09 (d, *J* 6 Hz, Pr^i), and 3·75 (sep, *J* 6 Hz, Pr^i)
(**2d**)	1·66 (s, Me) and C_6H_{11} obscure
(**2e**)	7·0—7·6 (m, Ph), 1·98 (s, Me), and 1·24 (s, Bu^t)
(**2f**)	7·35br (s, Ph), 1·23 (s, Bu^t), and Bu^n obscure[a]

[a] δ 2·05br (α-CH_2).

Although the decomposition of the iminodioxetans (**2a**)–(**2f**) gave no direct chemiluminescence, indirect chemiluminescence was observed in the presence of fluorescent molecules such as 9,10-diphenyl-(DPA) or 9,10-dibromo-anthracene (DBA). Analysis of the enhanced chemiluminescence showed that (**2a**)–(**2f**) each had a very low triplet-excitation yield $^3\phi$, *i.e.*, (**2a**) 3·4 × 10^{-5},[3] (**2b**) 1·6 × 10^{-4}, (**2c**) 1·4 × 10^{-4}, (**2d**) 8·0 × 10^{-5}, (**2e**) 3·1 × 10^{-4}, and (**2f**) 8·6 × 10^{-6}; $^3\phi/^1\phi > 500$ for (**2a**)–(**2f**).

---

† The decomposition of (**2a**)—(**2f**) was followed by the decay of 9,10-dibromoanthracene (DBA)-enhanced chemiluminescence or by ^1H n.m.r. monitoring.

The yield of acetophenone from (**2f**) indicates that the apparent value of $^3\phi$ is $> 4 \times 10^{-3}$ for (**2f**), very much larger than $^3\phi$ determined by the enhanced chemiluminescence ($8{\cdot}6 \times 10^{-6}$) This large discrepancy and the much stronger (36 times) chemiluminescence of (**2e**) compared with (**2f**) suggest that (**2f**) decomposes *via* a biradical intermediate (**8**)[5] Experimental evidence also supports the biradical mechanism for the decomposition of (**6**) and (**7**).[2,6]

The sum of the activation energy and the reaction enthalpy for the decomposition of (**2a**), which approximates to the energy of the transition state above the ground state products, was estimated to be 92 kcal/mol,[3] which is smaller than that for (**6**) (97 kcal/mol)[7] or (**7**) (113 kcal/mol).[7] Thus, the low energy of the transition state for the decomposition of (**2a**) may be responsible for the very small excitation yield of (**2a**) ($^3\phi$ $3{\cdot}4 \times 10^{-5}$)[3] Recently, Schuster indicated that the increase in the ratio of triplet to singlet excitation yields ($^3\phi$ $^1\phi$) parallels the decrease of transition state energy[7] In line with this, the triplet to singlet ratios of (**2a**), (**6**), and (**7**) were 650,[3] 200,[7] and 15,[7] respectively It should also be noted that the decomposition of (**2e**), whose corresponding carbonyl product (acetophenone) has a lower triplet energy than aliphatic ketones, gave the highest value of $^3\phi$

We thank the Ministry of Education of Japan and the Kawakami Foundation for financial support

(*Received*, 16*th May* 1980, *Com* 531)

[1] For Part **122** of the Series Photoinduced Reactions, see I Saito, K Shimozono, S Miyazaki, and T Matsuura, *Tetrahedron Lett* , 1980, 2317

[2] For a review, see K A Horn, J -Y Koo, S P Schmidt, and G B Schuster, *Mol Photochem* , 1978—1979, **9**, 1

[3] Y Ito, T Matsuura, and H Kondo, *J Am Chem Soc* , 1979, **101**, 7105

[4] W Adam, O D Lucchi, H Quast, R Recktenwald, and F Yany, *Angew Chem* , *Int Edn Engl* , 1979, **18**, 788

[5] Y Ito, T Matsuura, and H Yokoya, *J Am Chem Soc* , 1979, **101**, 4010

[6] W Adam and F Yany, *Photochem Photobiol* , 1980, **31**, 267

[7] S P. Schmidt and G B Schuster, *J Am Chem Soc* , 1980, **102**, 306