Phosphorescence of Medium-sized Cycloalkanones

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Summary Compared with other saturated ketones, medium-sized cycloalkanones exhibit phosphorescence of unusually high quantum efficiencies.

MEDIUM-SIZED cycloalkanones (C_8—C_{11}) exist in unusual conformations which have a profound effect on their chemical behaviour. N.m.r. spectroscopy of these ketones over a wide range of temperature indicates that transannular interaction between the carbonyl and the appropriate methylene group across the ring may be important from ambient temperature down to −160 °C.[1] Alkanones undergo Norrish Type I, Type II, and related processes photochemically, while medium-sized cycloalkanones may also undergo transannular hydrogen abstractions to form bicyclic alcohols.[2] The predominant photochemical reaction of cyclodecanone is the formation of 9-decalols which occurs mainly from its $^3n,\pi^*$ state.[3] In order to achieve a better understanding of the behaviour of photoexcited medium-sized cycloalkanones, we investigated the influence of structure on the phosphorescence lifetimes and quantum yields of alicyclic and acyclic ketones and found that medium-sized cycloalkanones exhibit unusually high quantum yields of phosphorescence at 77 K.

20 cyclic and acyclic ketones were examined. The phosphorescence quantum yields (ϕ_p) and lifetimes (τ_p) of these ketones (0·01—0·5 M) in ether–isopentane–alcohol glasses were measured at 77 K on a Perkin–Elmer MPF-4 Corrected Spectrofluorimeter with phosphorescence attachment. The rates of phosphorescence, k_p, and non-radiative decay, k_{-t}, were calculated (Table). Although k_p is constant within a factor of 2—3, k_{-t} depends dramatically on the structure of these ketones. While cyclopentanone, cyclohexanone, and the linear ketones have non-radiative rates of 700—1600 s^{-1}, the medium-sized cycloalkanones have much smaller rates, ranging from 130 to 250 s^{-1}. In other words, the high ϕ_p of medium-sized cycloalkanones is due to their anomalously low k_{-t}. The predominant mode of decay of most photoexcited aliphatic ketones at 300 K is photochemical transformation which is effectively 'frozen out' at very low temperatures. At 77 K k_{-t} may consist solely of physical deactivation. The physical non-radiative decay of the $^3n,\pi^*$ state to the ground state of ketones is governed by the Franck–Condon factor which is related to the geometry of the $^3n,\pi^*$ state and that of the vibrationally excited ground state.[4] It is interesting that

TABLE

Ketone[a]	λ_{max}[b] /nm	τ/ms[c]	ϕ_p[d]	k_p[e]	k_{-t}[f]
Cyclopentanone	460	1·2	0·11	92	740
Cyclohexanone	480	0·9	0·064	68	1500
Cycloheptanone	440	2·7	0·33	120	250
Cyclooctanone	435	3·7	0·42	110	200
Cyclononanone	430	4·3	0·41	95	140
Cyclodecanone	435	4·3	0·44	100	130
Cycloundecanone	440	5·0	0·36	72	130
Cyclododecanone	445	3·1	0·37	120	200
Cyclotridecanone	440	4·7	0·31	66	150
Cyclopentadecanone	440	4·4	0·30	67	160
Acetone	460	0·6, 0·6[g] 0·4,[i] 0·33[j]	0·042, 0·043,[h] 0·03[i]	71	1600
Pentan-2-one	460	0·8	0·096	120	1100
Pentan-3-one	460	1·1, 1·26[g]	0·10	91	820
Hexan-2-one	460	0·7	0·093	130	1300
Hexan-3-one	460	1·0	0·079	79	920
Heptan-4-one	460	1·0	0·070	70	930
Octan-2-one	450	1·0	0·13	130	870
Octan-4-one	460	1·0	0·067	67	930
Adamatan-2-one	—	—	<0·005	—	—
2,2,4,4-Tetramethylpentan-3-one	460	6·7, 8·6[g]	0·29, 0·89[j]	43	110

[a] All values are for phosphorescence only. [b] ±5 nm. [c] ±0·1 ms. [d] Based on the phosphorescence of benzophenone, ϕ_p = 0·84, as the secondary standard, S. L. Murov, Ph.D. Thesis, University of Chicago, 1967. [e] Calculated from $k_p = \phi_p\tau^{-1}$. [f] Calculated from $k_{-t} = \tau_t^{-1} - k_p$. [g] D. S. McClure, *J. Chem. Phys.*, 1949, **17**, 905. [h] E. H. Gilmore, G. E. Gibson, and D. S. McClure, *ibid.*, 1952, **20**, 829; 1955, **23**, 399. [i] R. F. Borkman and D. R. Kearns, *ibid.*, 1966, **44**, 945. [j] M. O'Sullivan and A. C. Testa, *J. Amer. Chem. Soc.*, 1970, **92**, 258.

the phosphorescence maxima of medium-sized cycloalkanones occur at considerably shorter wavelengths than those of other saturated ketones, which may indicate that the geometry of the $^3n,\pi^*$ state of these cycloalkanones resembles more closely that of the lower vibrational levels of the ground state, resulting in a poorer Franck–Condon factor for non-radiative decay.† The unusual conformations of medium-sized cycloalkanones apparently alter the geometry of the excited carbonyl group, causing the dramatic increase in ϕ_p.

It is interesting that the k_p and k_{-t} values of 2,2,4,4-tetramethylpentan-3-one are similar to those of the medium-sized cycloalkanones, but ϕ_p (0·29) is appreciably less than that reported in the literature.[5] Our results suggest that substitution of α-H by Me is not the only important factor in determining the rate k_{-t} for ketones.[5] On the other hand, admantanone exhibits no detectable phosphorescence. In view of its photochemical stability at room temperature[6] this result must be attributed to its effective non-radiative decay.

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† Medium-sized cycloalkanones also absorb at longer wavelength and fluoresce at shorter wavelength than other saturated ketones, *e.g.*, cyclodecanone exhibits a λ_{max} (absorption) 290 nm and λ_{max} (fluorescence) 390 nm, while values for acetone are 278 and 415 nm, respectively.

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