

very little conjugation is present in the remaining ring systems. The C(10)-C(11) and the C(2)-C(3) double bonds are virtually isolated double bonds (1.31 (2) and 1.34 (1) Å, respectively) as is the C(12)-N(13) double bond (1.27 (1) Å).⁶ Furthermore conjugation is insignificant between the C(2)-C(3) double bond and the β -lactam ring system (C(2)-N(1) 1.40 (1) Å). The β -lactam ring is close to perpendicular to the plane of the indolenine system, the dihedral angle C(14)-C(19)-C(20)-C(21) is 120 (1)°. The distance between the imidazole N(7) and the carbonyl O in the ethyl acetate is 2.82 (2) Å indicating a strong hydrogen bond.

Biogenetically, chartelline A seems to be composed of modified tryptamine and histamine residues linked via an isoprene unit. The biosynthesis of this new class of alkaloids is at present totally unexplored as is the question whether chartelline A is a true bryozoan metabolite or originates with some symbiotic or associated organism. The chemical and biological properties of chartelline A and related natural products from bryozoans are at present being investigated.

Acknowledgment. We are pleased to acknowledge support from C.N.R.S. (Centre National de la Recherche Scientifique) and from CNEXO (Centre National d'Exploitation des Océans). We are indebted to Professor L. Cabioch, Station Biologique, Roscoff, for a generous gift of *C. papyracea* and to F. Hansen who greatly assisted in the collection of the diffractometer data. The Bruker HX-270 NMR spectrometer and the low-temperature equipment for the diffractometer (Grant 511-15102) were purchased by the Danish Natural Sciences Research Council to whom we are grateful for access to the instruments. We are grateful for very necessary financial support from the Thomas B. Thriges Foundation.

Registry No. (S)-Chartelline A, 96845-55-5.

Supplementary Material Available: Tables of structure factors, atomic coordinates, thermal parameters, bond angles, and bond lengths (4 pages). Ordering information is given on any current masthead page.

(6) The dihedral angle C(10)-C(11)-C(12)-N(13) is 104 (1)° and the torsion angle C(2)-C(3)-C(4)-N(5) is 113 (1)°.

Cyclization and Disproportionation Kinetics of Triplet Generated, Medium Chain Length, Localized Biradicals Measured by Time-Resolved CIDNP¹

Gerhard L. Closs* and O. David Redwine

Department of Chemistry, The University of Chicago
Chicago, Illinois 60637
Chemistry Division, Argonne National Laboratory
Argonne, Illinois 60439

Received January 8, 1985

With the advent of more reliable MO calculations and very fast experimental techniques the chemistry of biradicals has moved to the forefront of physical organic chemistry.² Ideally one would like to know static and dynamic properties associated with biradicals represented by a simple polymethylene chain, $\dot{\text{C}}\text{H}_2\text{-(CH}_2)_n\text{-}\dot{\text{C}}\text{H}_2$. Presumably because of experimental difficulties, no direct kinetic measurements have been reported for any of its members. In this paper we wish to report kinetics obtained for a series of compounds similar to polymethylenes except that one of the terminal methylenes is replaced by a carbonyl group. At present this series comes closest to the ideal mentioned above.

(1) Supported by NSF Grant CHE 8218164.

(2) Reviews on recent biradical chemistry: "Biradicals"; Borden, W. T., Ed., Wiley: New York, 1982. Scaiano, J. C.; Lissi, E. A.; Encina, M. V. *Rev. Chem. Intermed.* 1978, 2, 139. Scaiano, J. C. *Acc. Chem. Res.* 1982, 15, 252.

Scheme I

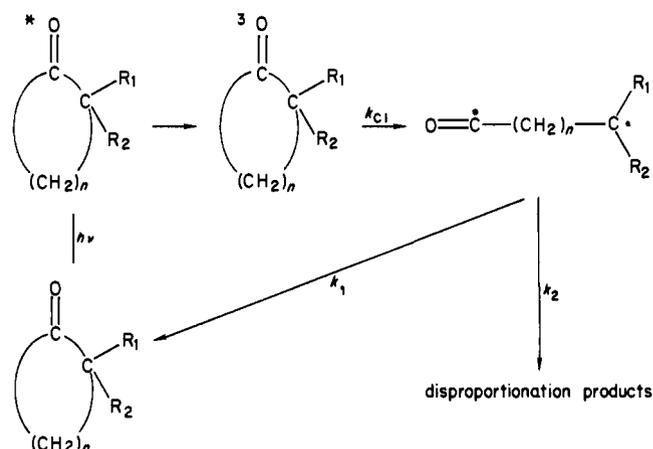


Table I

biradical	length	τ , ns ^a	disprop/ cycliz	EF ^b	(EF/ EF _{max})10 ²
$\dot{\text{C}}\text{H}_2\text{(CH}_2)_6\dot{\text{C}}\text{O}$ (1)	1,8	100	0.48	202	0.62
$(\text{CH}_3)_2\dot{\text{C}}\text{(CH}_2)_6\dot{\text{C}}\text{O}$ (2)	1,8	83	2.4	392	2.28
$\dot{\text{C}}\text{H}_2\text{(CH}_2)_2\dot{\text{C}}\text{O}$ (3)	1,7	100 (150) ^c	0.51	305	0.94
$\text{CH}_3\dot{\text{C}}\text{(CH}_2)_5\dot{\text{C}}\text{O}$ (4)	1,7	100	0.61	334	1.47
$(\text{CH}_3)_2\dot{\text{C}}\text{(CH}_2)_5\dot{\text{C}}\text{O}$ (5)	1,7	130	2.0	639	3.72
$\dot{\text{C}}\text{(CH}_2)_2\dot{\text{C}}\text{O}$	1,6	77	7.0	335	1.25

^aThe errors are estimated to be $\pm 20\%$. ^bEF, the enhancement factor is defined as the ratio of the CIDNP signal intensity, I , and the corresponding Boltzmann equilibrated signal, I^0 , at equal concentrations: $I/I^0 \times \text{conversion}$. Conversion is the fraction of the reactant converted to product per laser pulse. ^cFrom a biexponential fit it cannot be stated which exponent belongs to which reaction step. Both exponents are listed here.

The biradicals are generated by photolysis of cyclic ketones and the chemistry is represented by Scheme³ I. It is well established that intersystem crossing in ketones is very fast and that the cleavage occurs from a triplet state.⁴ In our work we measure the formation kinetics of the cyclic ketone and disproportionation products. In cases where cleavage (k_{c1}) is fast relative to the sum of the biradical decay rates, this yields directly the lifetime τ of the biradical ($1/\tau = k_1 + k_2$).

The experimental technique used is based on NMR detected laser flash photolysis recently developed in this laboratory.⁵ The method, an extension of CIDNP spectroscopy, samples the nuclear magnetization of the products formed after a time interval τ' between the laser pulse initiating the chemistry and the rf probing pulse. Only the magnetization of the diamagnetic products formed during τ' contributes to the spectrum. With our present equipment, operating at 60 MHz with a flip angle of 7° we are able to measure lifetimes as short as 25 ns.⁶ The advantage over faster optically detected flash photolysis lies in more positive product identification and the independence of the presence of a strong chromophore in the biradical.

The lifetime τ of the biradicals 1, 2, and 4-6 were obtained by fitting the formation rates of the products with a single ex-

(3) Norrish Type I generated phenyl substituted biradicals have been studied by flash photolysis by: Caldwell, R. A.; Sakuragi, H.; Majima, T. *J. Am. Chem. Soc.* 1984, 106, 2471.

(4) Heine, H. G.; Hartmann, W.; Kory, D. R.; Magyar, J. G.; Hoyle, E. C.; McVey, J. K.; Lewis, F. D. *J. Org. Chem.* 1974, 39, 691.

(5) Closs, G. L.; Miller, R. J. *J. Am. Chem. Soc.* 1979, 101, 1639; 1981, 103, 3586. Closs, G. L.; Sitzmann, E. V. *J. Am. Chem. Soc.* 1981, 103, 3217. Miller, R. J.; Closs, G. L. *Rev. Sci. Instrum.* 1981, 52, 1876.

(6) Deconvolution for the finite rf pulse width was accomplished by fitting the signal intensities to $I(\tau) = \int_0^\infty dc(t) \int_0^\infty F(t, \tau') dt$ where τ' is the delay between the laser pulse and the center of the rf pulse, $c(t)$ is the product concentration and $F(t, \tau')$ is the shape function of the rf pulse envelop.

ponential.⁷ This requires that the formation of the biradical is much faster than its decay ($k_{cl} \gg 1/\tau$). This assumption was checked by Stern-Volmer quenching experiments on the triplet states of the precursor ketones. With the exception of cycloheptanone all triplets have lifetimes of substantially less than 10 ns. The lifetime of **3** was obtained by fitting the data to a double exponential.

The results are summarized in Table I. The observed biradical lifetimes are relatively long and show not much variation within the series. As might be expected, branching of the alkyl end of the biradical increases the disproportionation to cyclization ratio. Although the structural variation within the series is not large, the small differences in τ and the long lifetimes suggest that the kinetics are controlled by spin dynamics.⁸

The last two columns in Table I give previously unavailable information on the mechanism of intersystem crossing in biradicals. To elaborate, it should be pointed out that in the absence of a magnetic field the eigenstates of biradicals of the type included here are close to pure singlets and triplets because the mixing interactions, V_{st} , are small compared to the singlet-triplet energy gap, $2J$.⁹ Time-dependent perturbation theory predicts the intersystem crossing rate constant ($k_{s,t}$) to be proportional to

$$k_{(s,t)} \propto V_{st}^2 / (V_{st}^2 + J^2)$$

An external magnetic field, B_0 (in our experiments $B_0 = 1.41$ T), changes this for the three triplet levels to

$$k_{s,t\pm} \propto V_{st}^2 / [V_{st}^2 + (2J \mp g\beta B_0)^2]$$

where β is the Bohr magneton and g the electron g factor. Since J is dependent on the conformation of the biradical which is itself time dependent, it can be seen that the rate is a complex function of the conformational dynamics, the magnitude of the field that determines the energy gap between the triplet levels and the singlet, and the magnitude of V_{st} .¹⁰

The last column of Table I lists the measured enhancement factors, EF for the disproportionation products as fractions of their maxima. Here EF_{max} is the computed enhancement obtained for a hypothetical biradical in which T_+ -S and all nuclear spin-independent mixing processes are negligible. The magnitude of EF_{max} is dependent on the number of protons carrying hyperfine interaction and, within the model, is independent of J . The results show that hyperfine interactions provide only a small fraction of the singlet-triplet mixing, with the major components coming from other mechanisms.¹² Two-center spin orbit coupling at the point of ring closure induced by the presence of an acyl function is a likely contributor.⁹ Within the series, the importance of the hyperfine mechanism increases with increased branching as evidence by a rise in EF/EF_{max} . This presumably reflects a larger hyperfine interaction in the branched compounds. Also, the importance of hyperfine-induced mixing is less in the 1,8 series than in the 1,7 series, in agreement with previous studies.⁹

In conclusion, it should be pointed out that the relatively long lifetime of triplet biradicals must be attributed to the poor energy match of singlet and triplet levels rather than to a lack of mixing interactions. It can be easily shown that for a radical pair in which triplet and singlet are strictly degenerate, the hyperfine interactions of typical alkyl radicals alone are large enough to cause intersystem crossing in less than 10 ns. We have confirmed this by attempting

to measure the geminate radical recombination resulting from the photolysis of dibenzyl ketone. The process is complete in less than 25 ns, the present time resolution of our experiment.⁶

Registry No. $\cdot\text{CH}_2(\text{CH}_2)_6\dot{\text{C}}\text{O}$, 69245-22-3; $(\text{CH}_2)_2\dot{\text{C}}(\text{CH}_2)_6\dot{\text{C}}\text{O}$, 96897-00-6; $\cdot\text{CH}_2(\text{CH}_2)_5\dot{\text{C}}\text{O}$, 96897-01-7; $\text{CH}_3\dot{\text{C}}\text{H}(\text{CH}_2)_5\dot{\text{C}}\text{O}$, 96897-02-8; $(\text{CH}_3)_2\dot{\text{C}}(\text{CH}_2)_5\dot{\text{C}}\text{O}$, 96897-03-9; $\dot{\text{C}}\text{H}_2\text{CH}_2\dot{\text{C}}\text{HCH}_2\text{CH}(\text{CH}_2)_2\dot{\text{C}}\text{O}$, 82352-63-4; cycloheptanone, 502-42-1; cyclooctanone, 502-49-8; 2,2-dimethylcycloheptanone, 7228-52-6; 2,2-dimethylcyclooctanone, 42393-51-1; 2-methylcycloheptanone, 932-56-9; 2-bicyclo[3.2.1]octanone, 5019-82-9.

The Direct Intermolecular Transfer of Dihydrogen between Two Transition-Metal Complexes

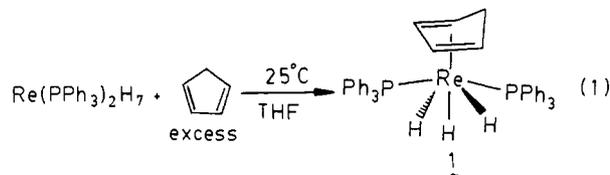
William D. Jones*† and John A. Maguire

Department of Chemistry, University of Rochester
Rochester, New York 14627

Received January 7, 1985

The reaction of dihydrogen with coordinately unsaturated 16-electron metal complexes in low oxidation states commonly leads to oxidative addition, a concerted process in which both hydrogen atoms are bound to the metal.¹ This process is often reversible, and reductive elimination of dihydrogen is also a common process. Only rarely have examples of hydrogen atom transfer from one metal to another been observed,² and cases in which two hydrogen atoms are transferred are even rarer.³⁻⁵ We present here evidence for the direct transfer of dihydrogen from rhenium to rhenium and rhenium to iridium.

In 1980, Ephritikhine and Felkin reported the preparation of $\text{CpRe}(\text{PPh}_3)_2\text{H}_2$ by treatment of $\text{Re}(\text{PPh}_3)_2\text{H}_7$ with a slight excess of cyclopentadiene in THF.⁶ The reaction was reported to proceed to completion in 15 min at 60 °C. Recently, we have found that $\text{Re}(\text{PPh}_3)_2\text{H}_7$ reacts with cyclopentadiene in THF (1:4 v/v) at 25 °C to give $(\eta^4\text{-C}_5\text{H}_6)\text{Re}(\text{PPh}_3)_2\text{H}_3$ (**1**) in high yield (eq 1).⁷



Compound **1**, isolated as colorless crystals, only slowly undergoes loss of dihydrogen at 60 °C to produce the dihydride complex $\text{CpRe}(\text{PPh}_3)_2\text{H}_2$ (**2**) ($\tau_{1/2} = 100$ min). The reluctance of **1** to undergo conversion to **2** at 60 °C seemed to rule out this species as an intermediate in the reaction of cyclopentadiene with $\text{Re}(\text{PPh}_3)_2\text{H}_7$ under the conditions employed by Ephritikhine and Felkin.

* Alfred P. Sloan Fellow, 1984-1986.

(1) Halpern, J. *Acc. Chem. Res.* **1970**, *3*, 386-392. Collman, J. P.; Hegedus, L. S. "Principles and Applications of Organotransitionmetal Chemistry"; University Science: Mill Valley, CA, 1980.

(2) See, for example: McCullen, S. B.; Brown, T. L. *J. Am. Chem. Soc.* **1982**, *104*, 7496-7500. Jones, W. D.; Huggins, J. M.; Bergman, R. G. *J. Am. Chem. Soc.* **1981**, *103*, 4415-4423. Lehnig, M. *Tetrahedron Lett.* **1977**, *41*, 3663-3666.

(3) Drouin, M.; Harrod, J. F. *Inorg. Chem.* **1983**, *22*, 999-1001. Harrod, J. F.; Yorke, W. J. *Inorg. Chem.* **1981**, *20*, 1156-1159.

(4) Johnson, C. E.; Fisher, B. J.; Eisenberg, R. *J. Am. Chem. Soc.* **1983**, *105*, 7772-7774. Johnson, C. E.; Eisenberg, R. *J. Am. Chem. Soc.*, **1985**, *107*, 3148-3160.

(5) Hazel, N. J.; Howard, J. A. K.; Spencer, J. L. *J. Chem. Soc., Chem. Commun.* **1984**, 1663-1664.

(6) Ephritikhine, M.; Felkin, H. *J. Organomet. Chem.* **1982**, *224*, 363-376. Baudry, D.; Ephritikhine, M. *J. Chem. Soc., Chem. Commun.* **1980**, 249-250.

(7) Jones, W. D.; Maguire, J. A. *Organometallics* **1985**, *4*, 951-953.

(7) The signal intensity in the 1,8 biradicals at early times in not proportional to the product formation because the triplet sublevels react with different rates and give different polarization patterns. This has been taken into account and will be explained in detail in a separate publication.

(8) This conclusion has been expressed previously by: Scaiano, J. C. *Tetrahedron* **1982**, *38*, 819.

(9) Closs, G. L. *Adv. Magn. Res.* **1974**, *1*, 157. Closs, G. L. *NATO Adv. Study Inst. Ser., Ser. C* **1979**, *34*, 225.

(10) The CIDNP spectra resulting from these dynamics have been modeled by: de Kanter, F. J. J.; den Hollander, J. A.; Huizer, A. H.; Kaptein, R. *Mol. Phys.* **1977**, *34*, 857. Doubleday, C., Jr. *Chem. Phys. Lett.* **1981**, *77*, 131; **1982**, *85*, 65.

(11) Nuclear spin independent processes are assumed to be negligibly small for the calculation of EF_{max} .

(12) This conclusion has been anticipated in ref 9 and by: de Kanter, F. J. J.; Kaptein, R. *J. Am. Chem. Soc.* **1982**, *104*, 4759.