(chlorobenzene) in the presence of 5 equiv of ethanol, the ester **22** (22%), carbamate **23** (32%), and 2-amino-3-chloro-N-phenylmaleimide (**21**)[10] (20%) were isolated. The ester and carbamate arise from ethanol addition to the respective cumulenes. The amino compound **21** is of particular note since its formation suggests that a nitrene may precede zwitterion formation and is trapped by hydrogen atom abstraction.

Acknowledgment. The authors wish to thank the National Science Foundation (MPS74-06932) for financial support of this work.

Dedication: This work is dedicated to Professor Harold R. Snyder in honor of his retirement after an illustrious career on the faculty of the University of Illinois, Champaign-Urbana.

References and Notes

(1) We have utilized this simple model to guide our previous work on the thermal chemistry of azidoquinones: H. W. Moore, *Chem. Soc. Rev.*, **2,** 415 (1973).

(2) Combustion analyses and mass spectral properties of all new compounds described here are in agreement with their formulations.

(3) γ-Methoxy-α,β-dichloro-$\Delta^{\alpha,\beta}$-crotonolactone (**7**) is a known compound (V. Zikan, L. Vrba, B. Kakac, and M. Semonsky, *Collect. Czech. Chem. Commun.*, 38, 1091 (1973)). The other compounds in this series, i.e., **8, 9,** and **10,** are new compounds and were identified from their spectral properties and combustion analyses.

(4) See, for example, T. I. Bobrova, S. D. Volodkovish, and S. S. Kukalenko, *Zh. Obsch. Khim.*, **44,** 390 (1974); F. Zanker and F. Reischeneder, German Patent, 2,053,073 (1973), *Chem. Abstr.*, **77,** 75020 (1972); E. Winterfeldt and J. M. Nelke, *Chem. Ber.*, **101,** 3163 (1968); M. Semonsky, N. Kucharczyk, V. Zikan, and V. Jelinek, Czechoslovak Patent, 145,820 (1972), *Chem. Abstr.*, **78,** 159241 (1973); S. Jung, L. Jung, and P. Cordier, *C.R. Acad. Sci. Ser C*, **262,** 1793 (1966); M. Semonsky, E. Rockova, V. Zikan, B. Kakac, and V. Jelinek, *Collect. Czech. Chem. Commun.*, **28,** 377 (1963).

(5) *E*-Stereochemistry of **13** and **15** is assumed. This is based upon the report that chloroketene cycloadds to imines to give primarily the *trans*-3-chloro-2-azetidinones: D. A. Nelson, *Tetrahedron Lett.*, 2543 (1971).

(6) A. Gomes and M. Jouille, *Chem. Commun.*, 935 (1967): H. B. Kagen and J. L. Lache, *Tetrahedron Lett.*, 3093 (1968); R. Huisgen, B. Davis, and M. Morikawa, *Angew. Chem. Int. Ed. Engl.*, **7,** 826 (1968); F. Duran and L. Ghosez, *Tetrahedron Lett.*, 245 (1970).

(7) H. W. Moore, H. R. Shelden, D. W. Deters, and R. J. Wikholm, *J. Am. Chem. Soc.*, **92,** 1675 (1970).

(8) H. W. Moore and H. R. Shelden, *J. Org. Chem.*, **33,** 4019 (1968).

(9) The azide was prepared in 77% yield by treating an acetonitrile solution of 2,3-dichloro-*N*-phenylmaleimide with 1 equiv of sodium azide, mp 113° dec.

(10) This compound was identified from its spectral properties and its independent synthesis by catalytic reduction of **20.**

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Oscillations in Chemical Systems. 15.[1] Deliberate Generation of Trigger Waves of Chemical Reactivity

Sir:

The oxidation of malonic acid by acidic bromate exhibits remarkable behavior when catalyzed by some 1-equivalent redox couples. Belousov[2] first observed homogeneous oscillations with the Ce(III)-Ce(IV) system, and Zhabotinsky[3] observed moving regions of alternating oxidation and reduction of the indicator catalyst ferrous phenanthroline.

Winfree[4,5] has studied the latter system in detail. When the solution is spread in a thin film saturated with air, the indicator may remain almost indefinitely in the reduced form without oxidation. However, this steady state situation is excitable, and reaction at a localized heterogeneous "pacemaker" can create a region of oxidation that then travels outward undamped at constant velocity as a thin band or trigger wave. Winfree[5] reports fascinating spirals and scrolls that can result from perturbation of these bands. Field and Noyes[6] measured band migration rates at different reagent concentrations and elucidated the mechanism of propagation. They also developed a model[7] of how the medium in the steady state could be excited by localized depletion of bromide ion.

The pacemakers observed by Winfree[4,5] were apparently adventitious dust particles, and he had no way to control the initiation of specific bands. Field and Noyes[6] found that nichrome wire could act as a pacemaker broadcasting repetitive pulses at a definite frequency. However, they still had no control over initiating individual pulses of oxidation. We report here a system in which such pulses can be generated at will.

Silver seemed a logical reagent to involve in local depletion of bromide ion, and we found that either a small crystal of silver nitrate or a piece of silver wire acted as an excellent pacemaker and generated successive waves of chemical activity. However, the pacemaking activity of a silver wire electrode could be suppressed by biasing it negative with respect to a platinum electrode in the same solution. The negative bias obviously suppresses the reaction $Ag(s) + Br^-(aq) \rightarrow AgBr(s) + e^-$.

If such a biased silver electrode is pulsed positive by a square wave lasting a few milliseconds, the oxidizing region that is generated moves outward as a trigger wave. The duration of the pulse necessary to generate such a wave is reduced if the pulse potential is more positive, and it is a fairly reproducible function of reactant concentrations. For the experiments at 25 °C reported here, trigger waves were suppressed by a negative bias of 0.6 V, and square wave pulses were 2.0 V positive.

The critical pulse width necessary to initiate a trigger wave varied between 1 and 7 ms and decreased linearly with increasing concentration of either H_2SO_4 or $NaBrO_3$. Extrapolations suggested the critical pulse width would go to zero either at $[BrO_3^-] = 0.12$ M, $[H_2SO_4] = 0.37$ M or at $[BrO_3^-] = 0.075$ M, $[H_2SO_4] = 0.60$ M. If $[BrO_3^-][H_2SO_4] \geqslant 0.045$ M^2, the 0.6-V negative bias apparently can no longer suppress pacemaking activity.

When critical pulse widths were plotted against concentrations of malonic acid, ferrous phenanthroline, or bromomalonic acid, the best lines through the points were horizontal or had slightly positive slopes; these reagents either have no effect on or slightly inhibit trigger wave generation. These results are consistent with our previous conclusions that both the rate of autocatalytic generation of bromous acid[8,9] and the rate of trigger wave propagation[6] depend only upon the product $[H^+][BrO_3^-]$ and not upon other concentrations.

Following a pulse of duration t, an ion reacting at an electrode should exhibit an approximately linear concentration gradient for a distance $2(Dt/\pi)^{1/2}$ where D is the diffusion coefficient. We have previously[6] estimated D for Br^- to be 1.8×10^{-5} cm^2 s^{-1}. Then a pulse of 4 ms would influence bromide concentration for a distance of about 3 μm; this distance is comparable to the calculated[6] width of the band front in an advancing trigger wave.

We also measured the voltage drop across a 100 ohm resistance in series with the electrode. The current during the pulse was about 0.6 mA and the electrode area was about 0.016 cm^2. This current is about 10^4 times that sufficient to deplete all of the estimated[6] 4×10^{-7} M bromide ion in the zone of possible influence, and it is obvious that other species contributed to reaction at the electrode.

A trigger wave from a pulsed silver electrode can be directed down a channel in a Teflon waveguide at a rate of the order of millimeters per minute as measured previously.[6] When the wave reaches a platinum electrode, it will generate a response that can be introduced as a signal to an electronic circuit. We therefore have a homogeneous solution that can model a situation very like a nerve axon in that a controlled input at one point can generate a wave of chemical activity that moves unidirectionally at a known rate and delivers a signal to another predetermined point with a predictable delay.

The observations reported here reinforce our previous[6,7,9] mechanistic interpretation of this system. We shall publish a more complete account after we have investigated the variation of critical pulse width as a function of the potentials at which the electrode is pulsed and biased and as a function of the time since the last trigger wave. Because a trigger wave propagates at a rate influenced by the time since passage of the preceding wave, the spacings of pulses received at the platinum electrode should differ in predictable ways from the spacings between the initiating pulses.

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Supplementary Material Available: Detailed experimental procedures for those wishing to reproduce our observations (1 page). Ordering information is given on any current masthead page.

References and Notes

(1) Paper No. 14 is R. M. Noyes, *J. Chem. Phys.*, in press.
(2) B. P. Belousov, *Ref. Radiat. Med.*, 145 (1959).
(3) A. N. Zaikin and A. M. Zhabotinsky, *Nature (London)*, **225**, 535 (1970).
(4) A. T. Winfree, *Science*, **175**, 634 (1972).
(5) A. T. Winfree, *Science*, **181**, 937 (1973).
(6) R. J. Field and R. M. Noyes, *J. Am. Chem. Soc.*, **96**, 2001 (1974).
(7) R. J. Field and R. M. Noyes, *Faraday Symp., Chem. Soc.*, **9**, 21 (1974).
(8) R. M. Noyes, R. J. Field, and R. C. Thompson, *J. Am. Chem. Soc.*, **93**, 7315 (1971).
(9) R. J. Field, E. Koros, and R. M. Noyes, *J. Am. Chem. Soc.*, **94**, 8649 (1972).

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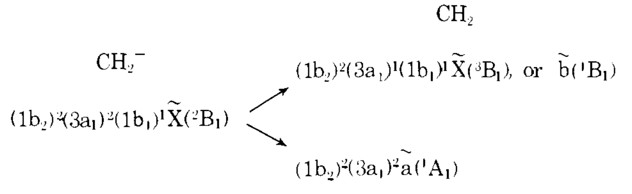
Laser Photoelectron Spectrometry of CH_2^-. Singlet–Triplet Splitting and Electron Affinity of CH_2[1]

Sir:

Laser photoelectron spectrometry of CH_2^- has been utilized to determine the electron affinity (EA) and the intercombination ($^1A_1 \leftarrow {}^3B_1$) energy difference in methylene. These experimental results, coupled with ab initio calculation, and a Franck–Condon factor analysis have enabled construction of accurate potential surfaces for $CH_2^-(^2B_1)$ and $CH_2(^3B_1)$ and ($^1A_1$). The $^3B_1$ ground state of methylene is found to be bent with ∠HCH of 138 ± 4°, and the intercombination separation is 0.845 ± 0.03 eV (19.5 ± 0.7 kcal/mol).

The experimental method employed consists of crossing a mass-analyzed CH_2^- ion beam with an argon ion laser operating at 488 nm (2.540 eV). The CH_2^- ions are extracted from discharges in both CH_4 and CH_2N_2 gas at ~1 Torr. Those photodetached electrons that enter the acceptance aperture of a hemispherical electrostatic monochromator are energy analyzed and counted. The electron binding energies are obtained to a first approximation[2] by subtracting the measured electron kinetic energy from the laser photon energy. The absolute electron energy scale is determined by simultaneous photodetachment of CH_2^- and O^-, the latter EA being well known.[3]

The CH_2^- photoelectron spectrum results from one-electron, dipole allowed transitions between the ground electronic state of CH_2^- and the several low lying states of CH_2. The CH_2^- ion possesses the same symmetry and molecular orbital configuration as the isoelectronic species NH_2: $(1b_2)^2(3a_1)^2(1b_1)^2\tilde{X}(^2B_1)$. From this state, the following low energy transitions are possible.



$$\begin{tikzcd}[column sep=small] \mathrm{CH_2^-} & \mathrm{CH_2} \\ & (1b_2)^2(3a_1)^1(1b_1)^1\tilde{X}(^3B_1),\ \text{or}\ \tilde{b}(^1B_1) \\ (1b_2)^2(3a_1)^2(1b_1)^1\tilde{X}(^2B_1) \arrow[ru] \arrow[rd] & \\ & (1b_2)^2(3a_1)^2\tilde{a}(^1A_1) \end{tikzcd}$$

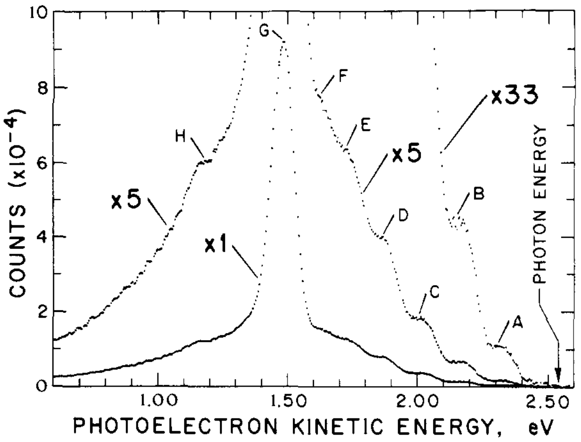


Figure 1. Experimental photoelectron spectrum of CH_2^-.

Past work[4] on OH^-, CH^-, SiH^-, and SiH_2^- indicates that the ground state geometries of hydride negative ions are very similar to those of their neutral isoelectronic neighbors. Comparing with NH_2, we thus expect the structure of $CH_2^-(^2B_1)$ to be $r_e \approx 1.1$ Å, and $\theta_e \approx 100°$. This conclusion has been verified with a double zeta configuration interaction calculation of the CH_2^- geometry. The spectroscopically obtained[5] structure of $\tilde{a}\ {}^1A_1$ CH_2 is $r_e \sim 1.11$ Å, $\theta_e = 102.4°$. Thus the ejection of the CH_2^- nonbonding $1b_1$ electron results in production of $CH_2(^1A_1)$ with a virtually identical geometry. Franck–Condon factors allow essentially only diagonal ($\Delta v = 0$) transitions and a single intense peak is expected in the photoelectron spectrum of this state. In contrast, transitions to the $^3B_1$ and $^1B_1$ states involve ejection of an electron from a $3a_1$ orbital with more bonding character and a large geometry change, such that an extended bending vibrational progression is expected for these states.

The observed photoelectron spectrum of CH_2^- (Figure 1) is in accord with these expectations. The prominent peak, G, is assigned as the transition to $v = 0$, $CH_2(^1A_1)$; the much weaker peaks A → F spaced at approximately 1200 cm^{-1} are assigned as a bending progression. The apparent regularity of this progression coupled with a constant photoelectron angular distribution over the peaks A → F (differing markedly from that for peak G) and the theoretical Franck–Condon analysis discussed below allows unambiguous assignments of peaks A → F as the $^3B_1$ CH_2 bending progression. The possibility of CH_2^- hot bands is ruled out by the identical photoelectron spectra produced from parent CH_4 or CH_2N_2.

A similar spectrum results from photodetachment of CD_2^- ions; the spacing of the 1200-cm^{-1} progression drops to about 900 cm^{-1} and the single peak "G" essentially does not move. The isotope shift can be used to obtain the vibrational level numbering in the long progression. Based upon these shifts, the only possible identification for the transition "A" is $v = 0$ of $CH_2(^3B_1)$. After small corrections for energy scale nonlinearities and rotational effects, the following direct experimental results are obtained:

$$\mathrm{EA}(CH_2) = (0.210 \pm 0.03)\ \mathrm{eV}$$

$$\Delta E(^1A_1 \leftarrow {}^3B_1) = (0.845 \pm 0.03)\ \mathrm{eV}$$

The present value for the intercombination splitting (19.5 ± 0.7 kcal/mol) is significantly higher than most photochemical estimates. These studies place the $^1A_1$ state above the $^3B_1$ state by about 1–8 kcal/mol.[6] Theoretical computations of this singlet–triplet splitting were initially reported to be 24 kcal/mol but over the past 15 years increasingly sophisticated computational efforts[7] have yielded an extrapolated value of 10–12 kcal/mol.

To confirm the above interpretations, ab initio calculations