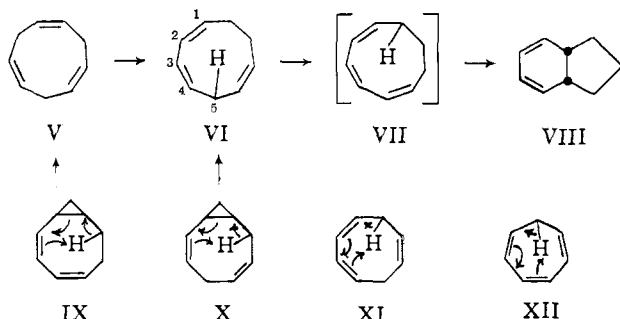I II III IV

25–50° is relatively rapidly converted first to A and then to B, these materials being distinguished by v.p.c. More vigorous treatment at 75° gives rise to one or more additional materials in a new v.p.c. fraction C. Pure fractions A and B were obtained most simply by preparative v.p.c. of isomerization mixtures after 7 min. at 25° or 25 min. at 50°, respectively.

TABLE I

ISOMERIZATION OF V BY POTASSIUM t-BUTOXIDE IN DMSO

Time, min.	T, °C.	V	A	B	C
5	25	45	52	3	
7	25	12	77	10	1
5	50		51	46	3
25	50		8	86	6
60	75		5	42	53

Examination of material A showed it to be *cis-cis-cis*-1,3,6-cyclononatriene (VI). Its n.m.r. spectrum showed proton signals at 4.23 τ (vinyl), 7.4 (bisallylic), and 7.96 (allylic) with relative areas of 3.02:1.00:1.98, respectively. In its infrared spectrum, it displayed bands at 1645 and 1627 cm.$^{-1}$ for isolated and conjugated olefinic stretching vibrations, strong bands at 670 and 717 for *cis*-olefinic C–H out-of-plane deformation, and no bands corresponding to C–H deformation characteristic of *trans*-olefins. In 95% ethanol solvent, VI displays an ultraviolet absorption band at 223 mμ (ϵ 3890) with strong absorption at longer wave lengths (ϵ 2090 at 240 mμ.) The ultraviolet, infrared, and n.m.r. spectra of VI agree very well with those observed by Roth[3] on a 1,3,6-cyclononatriene sample obtained by thermal isomerization of the 1,3,6-cyclooctatriene monomethylene adduct(X).

V VI VII VIII

IX X XI XII

Examination of material B showed it to be *cis*-bicyclo-[4.3.0]nona-2,4-diene (VIII). Its infrared spectrum was essentially identical with the spectrum of VIII published by Alder and Dortmann.[4] It contained none of the bands unique to the *trans* isomer of VIII, also reported by these authors.[4] The ultraviolet spectrum of B ($\lambda_{max}^{95\%\ EtOH}$ 263 mμ (ϵ 3000)) and its n.m.r. spectrum (4.00:2.04:2.10:4.09 ratio of vinyl:allylic: methylene: methylene protons at 4.37, 7.34, 7.92, and 8.56 τ, respectively) are consistent with the *cis*-bicyclo-[4.3.0]nona-2,4-diene structure VIII.

From Table I, it is clear that 1,3,6-cyclononatriene (VI), the first isomerization product derived by removal of an allylic proton from 1,4,7-cyclononatriene and re-addition to a new carbanionic carbon atom, is an intermediate on the way to the bicyclic isomer (VIII). Consistently, treatment of isolated VI with 1.2 M KOBu in DMSO for 60 min. at 25° in a separate experi-

(3) W. Roth, private communication; *Ann.*, in press.
(4) K. Alder and H. A. Dortmann, *Ber.*, **87**, 1905 (1954).

ment converted *ca.* 75% of it to VIII, together with a small proportion of C.

The most likely route between VI and VIII, but not the only conceivable one, involves further isomerization of VI to *cis-cis-cis*-1,3,5-cyclononatriene (VII) and rapid conversion of the latter to its valency tautomer[5] (VIII). The failure to detect the 1,3,5-isomer (VII) during the isomerizations does not militate against it as an intermediate since the isomerization was followed only by v.p.c. and the valency isomerization of VII to VIII could be expected to be quite rapid and very complete, judging by rates and equilibrium in the analogous valency tautomerism between 1,3,5-cyclooctatriene and its bicyclic isomer.[7,8]

It seems most probable that the isomerizations of 1,2,6-cyclononatriene observed by Gardner[1] also proceed by way of *cis-cis-cis*-1,3,6-cyclononatriene (VI) as the first intermediate and then follow the course observed in the present work with 1,4,7-cyclononatriene.[9] With 1,2,6-cyclononatriene, Gardner followed the isomerization to later stages than was done with the 1,4,7-isomer. Under these conditions, VIII presumably gives rise to II by way of at least one other isomer.

It is interesting that isomerization of 1,3,6-cyclononatriene (VI) to bicyclic isomer can also be accomplished thermally. While this thermal isomerization has been examined only in a preliminary way, the indications are that it occurs at a convenient rate at 200°. Presumably this involves a dienyl 1,5-hydrogen shift leading to 1,3,5-cyclononatriene, the latter undergoing valency isomerization. The dienyl 1,5-shift is analogous to dienyl and homodienyl 1,5-shifts in 1,3,6-octatriene[8] (XI), tropilidene[10] (XII), 1,3,5-cyclooctatriene mono-methylene adduct[3,8] (IX), and the 1,3,6-cyclooctatriene monomethylene adduct[3] (X).

(5) Analogously, *cis-cis-trans*-1,3,5-cyclononatriene was presumed by Alder[4] to be the precursor of the *trans* VIII obtained from Hofmann degradation on 1-dimethylamino-2,4-cyclononadiene. As Vogel[6] has pointed out, the evidence for the presumed valency isomerization is far from compelling, since a transannular elimination route is conceivable.

(6) E. Vogel, *Angew. Chem.*, **74**, 829 (1962).

(7) A. C. Cope, *et al.*, *J. Am. Chem. Soc.*, **72**, 2515 (1950); **74**, 4867 (1952).

(8) D. S. Glass, J. Zirner, and S. Winstein, *Proc. Chem. Soc.*, 276 (1963).

(9) Gardner, *et al.* (private communication, September 30, 1963), have now re-examined the material previously described[1] as 1,3,6-cyclononatriene and have found none of its chemistry consistent with data reported earlier.[1] Thus, the material which proved not to be an intermediate in the isomerization of 1,2,6-cyclononatriene was not the 1,3,6-isomer. Gardner, *et al.*, have now also identified VIII as one of the "short-lived intermediates" in the isomerization of 1,2,6-cyclononatriene.

(10) A. P. ter Borg, H. Kloosterziel, and N. Van Meurs, *Proc. Chem. Soc.*, 359 (1962).

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Effects of Millimolar Concentrations of Silver(I) Ion upon the γ-Radiolysis of Crystalline Potassium Nitrate

Sir:

The kinetics of formation of "equivalent nitrite," $M(NO_2^-)$, have been determined in pure and in silver-doped KNO_3, prepared by cocrystallizing mixtures of $AgNO_3$ and KNO_3, containing 0.04, 0.10, 0.4, and 1.0 mole % of Ag^+. Samples were irradiated in equipment described elsewhere[1] and products determined by dissolution at 20° in aerated water, followed by Shinn's analysis for nitrite.[2] Dissociation fragments, NO_2^-, NO_2, or NO, could each contribute to the observed total product,[3] which is expressed as moles of

(1) J. Cunningham, *J. Phys. Chem.*, **65**, 628 (1961).
(2) M. B. Shinn, *Ind. Eng. Chem., Anal. Ed.*, **13**, 33 (1941).
(3) J. Cunningham, *J. Phys. Chem.*, **67**, 1772 (1963).

nitrite ions, $M(NO_2^-)$, equivalent to the observed optical density change. Linear calibration plots *vs.* standard nitrite were unaffected by addition of unirradiated $(KNO_3 + Ag^+)$ or $(NaNO_3 + Ag^+)$, showing that neither the factor to convert optical density to $M(NO_2^-)$ nor the reproducibility $(\pm 1\%)$ of the analysis was affected by the presence of Ag^+ in the samples.

The growth of $M(NO_2^-)$ with dose is illustrated in Fig. 1 for KNO_3, $(KNO_3 + 0.04\% \ Ag^+)$, and $(KNO_3 + 0.1\% \ Ag^+)$ irradiated under continuous evacuation at $20°$. Maximum decompositions in Fig. 1 correspond to *ca.* 1% of NO_3^- ions converted to $M(NO_2^-)$, which appears to increase linearly with dose over this small decomposition range. In Fig. 2, curve A, data for pure KNO_3 γ-irradiated to greater than 1.5% decomposition at $20°$ are displayed as a first-order type plot of $-\log [1 - M(NO_2^-)]$ *vs.* dose. Date are represented within experimental error by two linear plots intersecting at 1.2% conversion, in good agreement with previous investigations.[4,5] The data for $(KNO_3 + 1.0\% \ Ag^+)$ in Fig. 2, curve C, show no evidence of a discontinuity in the presence of 1 mole $\%$ of Ag^+ centers, and dissociation obeys first-order kinetics to the highest decompositions studied. For $(KNO_3 + 0.4\% \ Ag^+)$ curve B, Fig. 2, shows that a kinetic "break" is observed but is less pronounced than in pure KNO_3 because the initial slope is lower. Relative to pure KNO_3, the initial slopes were 0.93, 0.86, 0.83, and 0.76 for salts prepared by the cocrystallization of KNO_3 with 0.04, 0.1, 0.4, and 1.0 mole $\%$ of Ag^+, respectively.

Two mechanisms could account for the observed efficiency of millimolar concentrations of Ag^+ in reducing initial radiolysis: (A) Each strongly polarizing Ag^+ center may reduce the probability of dissociation of *ca.* one thousand neighbors by "energy localization" processes, in which excitation energy normally mobile through the crystal (*e.g.*, excitons) may be trapped near Ag^+ and dissipated without dissociation. Katsuura and Inokuti have concluded from calculations on a one-dimensional model that conditions for localization of excitation energy can occur around an impurity center.[6] (B) Dissociative electron attachment (DEA) processes involving secondary electrons moderated to nearly thermal energies—as investigated by Hamill, *et al.*, for organic glasses[7,8]—may be reduced because Ag^+ centers scavenge the low-energy electrons. E.p.r.[9,10] and optical[11] studies have provided evidence for electron attachment to NO_3^- during irradiation at 77 and $4.2°K$. and recent work[12] has shown that millimolar Ag^+ competes for available electrons in $(KNO_3 + Ag^+)$ irradiated at $77°K$. However, electrons photodetached from trapping sites after γ-irradiation[3] at $77°K$. did not change $M(NO_2^-)$. The detailed form of mechanism B required by these experimental results would be that Ag^+ reduces initial radiolysis at $300°K$. by providing sites at which electrons, encountering one Ag^+ center in 10^2–10^3 lattice sites visited, remain trapped for a mean lifetime greater than that taken for excited intermediates to decay to their ground states without DEA. Present results provide indirect evidence, as follows, that if the latter mechanism be ac-
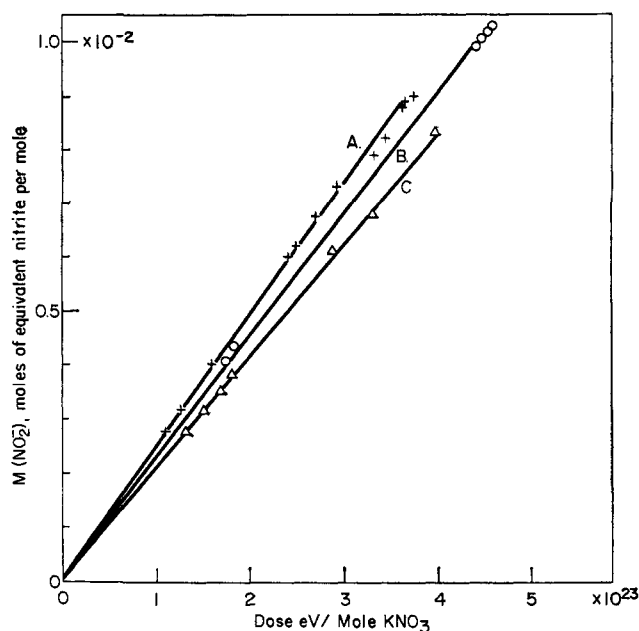
(4) J. Cunningham and H. G. Heal, *Trans. Faraday Soc.*, **54**, 1355 (1958).

(5) E. R. Johnson and J. Forten, *Discussions Faraday Soc.*, **31**, 238 (1961).

(6) K. Katsuura and M. Inokuti, *J. Phys. Soc. Japan*, in press.

(7) J. P. Guarino, M. R. Ronayne, and W. H. Hamill, *Radiation Res.*, **17**, 379 (1962).

(8) W. H. Hamill, J. P. Guarino, M. R. Ronayne, and J. A. Ward, *Discussions Faraday Soc.*, in press.

(9) J. Cunningham, *J. Phys. Chem.*, **66**, 779 (1962).

(10) C. Jaccard, *Phys. Rev.*, **124**, 60 (1961).

(11) J. Cunningham, *J. Phys. Chem. Solids*, **23**, 843 (1962).

(12) J. Cunningham, *ibid.*, in press.

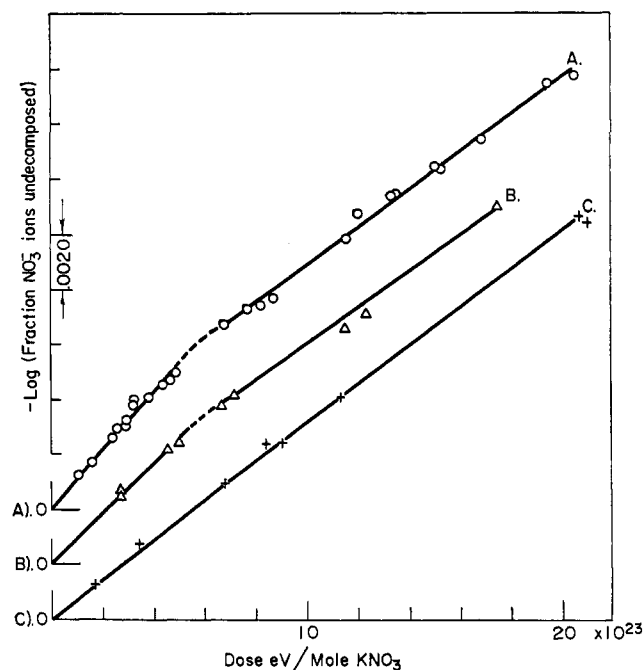Fig. 1.—Low dose γ-radiolysis of (A) KNO_3, (B) $(KNO_3 + 0.04\% \ Ag^+)$, (C) $KNO_3 + 0.1\% \ Ag^+$.

Fig. 2.—Data for (A) KNO_3, (B) $KNO_3 + 0.4\% \ Ag^+$, (C) $KNO_3 + 1\% \ Ag^+$, displayed as first-order plots.

cepted as a working hypothesis, DEA contributes to only $(30 \pm 10)\%$ of all radiolysis events in KNO_3.

According to mechanism B, the initial rate constant, $k_{(Ag^+)}$, for radiolysis of $(KNO_3 + 1\% \ Ag^+)$ is lower than that for pure KNO_3 because a fraction, x, of low-energy electrons is scavenged by Ag^+. Least squares analysis of Fig. 2 data shows that first-order rate constants of KNO_3 and $(KNO_3 + 0.4\% \ Ag^+)$ above 8×10^{23} e.v. $mole^{-1}$ are closely equal (to $\pm 2\%$) to $k_{(Ag^+)}$. It is reasonable to conclude that the same fraction, x, of thermalized electrons is scavenged by centers other than Ag^+ in the latter salts above the kinetic discontinuity, which has been correlated by previous investigations[4,13] with the appearance of significant concentrations of interstitial molecular oxygen product. The exact role of O_2 in reducing the rate was

(13) J. Forten and E. R. Johnson, *ibid.*, **15**, 218 (1960).

not there established, but, since recent work[14] shows that electron attachment to O_2 is a fast process, the discontinuity may be attributed to electron attachment to molecular oxygen product with accompanying reduction in DEA. The identical reductions in rate by 1% Ag^+ and by interstitial molecular oxygen, alone or in combination with 0.4% Ag^+, are then most readily explained by total scavenging of low-energy electrons by these concentrations of Ag^+ and/or O_2. Maximum reductions of DEA processes would be predicted for $AgNO_3$ on mechanism B and, in fact, $G_{NO_3^-}$ experimental values for that salt fall $(30 \pm 10)\%$ below the value predicted from the linear relationship between "free-space" and log $G_{NO_2^-}$ for other univalent nitrates.[15]

We are continuing studies on the radiolysis of ionic solids to assess the relative importance of mechanisms A and B, and the possible role of localization and ionization of superexcited states close to impurity centers.

(14) S. Gordon, E. J. Hart, J. Matheson, and J. K. Thomas, *J. Am. Chem. Soc.*, **85**, 1375 (1963).

(15) J. Cunningham and L. R. Steele, *Phys. Rev. Letters*, **9**, 47 (1962).

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Cyclobutane Formation from Mercury-Photosensitized Reactions of Ethylene

Sir:

It is now generally agreed that Hg 6^3P_1 photosensitization of ethylene produces this molecule in one or more electronically excited states, presumably of triplet character.[1] Earlier work has not indicated a gross amount of C_4 products which might result from addition of a triplet diradical ethylene to a molecule of ethylene in the ground state[2,3]; knowledge of such reactivity of other triplet species, *e.g.*, oxygen and sulfur atoms,[4,5] toward double bonds indicated the possibility of an excited molecule addition reaction in low yield for triplet ethylene. In the work being reported here the photosensitized reactions of ethylene were reinvestigated at higher pressures and lower conversions than hitherto employed to obtain information concerning the bimolecular reactivity of the triplet ethylene.

Matheson Research Grade ethylene at pressures between 18 and 140 cm. was circulated through a closed loop system consisting of a mercury saturator and a trap at $0°$ to maintain a constant mercury pressure and then through a fused silica photolysis cell at *ca.* $30°$. After irradiation with a mercury resonance lamp, the pressure of noncondensible gas was measured to determine the extent of decomposition to hydrogen and acetylene. The photolyses were carried to a maximum of 0.1% decomposition to noncondensables. A primary product separation using a 0.5-in. diameter silicone oil on firebrick g.l.p.c. column at $0°$ removed the bulk of the unreacted ethylene. The C_4 and higher product mixture, obtained by heating and backflushing this column, was then subjected to g.l.p.c. analysis using a flame ionization detector. Silicone oil and silver nitrate in glycerol columns, whose temperatures were separately variable, were operated in series. A low holdup grease-free valve before the flame permitted the rescue of selected larger peaks for mass spectra.

(1) D. W. Setser, B. S. Rabinovitch, and D. W. Placzek, *J. Am. Chem. Soc.*, **85**, 862 (1963).

(2) B. de B. Darwent, *J. Chem. Phys.*, **20**, 1673 (1952).

(3) J. R. Majer, B. Mile, and J. C. Robb, *Trans. Faraday Soc.*, **57**, 1342 (1962).

(4) R. J. Cvetanović, *Can. J. Chem.*, **38**, 1678 (1960).

(5) O. P. Strausz and H. E. Gunning, *J. Am. Chem. Soc.*, **84**, 4080 (1962).

The principal products observed were butane, butene-1, butadiene, cyclobutane, hexene-1, and hexane. Acetylene is not eluted from the silver nitrate column.

The cyclobutane yield appeared to increase linearly with ethylene pressure, although the yields of the other products decreased roughly as the reciprocal of the ethylene pressure. Addition of 99 and 224 cm. of argon on two runs to reactant ethylene at a pressure of 18 cm. had the effect of decreasing the yields of all products except cyclobutane; the product mixture composition at 224 cm. of argon and 18 cm. of ethylene was typical of that observed with 36 cm. of ethylene alone. The low-voltage mass spectrum of the butene-1, produced from a run starting with 73 cm. of an ethylene mixture containing 32% C_2D_4, showed major contributions at $m/e = 63$ and at other mass numbers corresponding to an odd number of deuterium atoms in the parent molecule ion. It is concluded from this analysis that the bulk of the butene-1 is not produced by an intramolecular rearrangement of an ethylene dimer, which would yield butene-1 as C_4H_8, $C_4H_4D_4$, and C_4D_8, but must arise from radical addition and disproportionation processes involving vinyl and butenyl radicals. It is known that vinyl radicals are a product of the primary quenching process in small yield at lower ethylene pressures, but the importance of this mode of ethylene decomposition at the pressures employed in this study has not been reported previously. The ethylene fraction recovered from the work with the C_2H_4–C_2D_4 mixture was examined for the presence of $C_2H_2D_2$ which would result from the decomposition of cyclobutane $C_4H_4D_4$. Low-voltage mass spectra gave the $^{30}/_{32}$ mass ratio of 0.015 ± 0.001 for the reactant C_2D_4, and 0.015 ± 0.001 for the recovered ethylene mixture. This indicates that any $C_2H_2D_2$ formed was less than 0.1% of the C_2D_4 present. Analysis (g.l.p.c.) of this recovered ethylene mixture using a 100-ft. silver nitrate in glycerol column, which was capable of separating isotopically different ethylenes, further reduced the limit for $C_2H_2D_2$ content to less than 0.01%.[6] Measurements of relative quantum yields by Callear and Cvetanović[7] up to 74 cm. may be combined with Darwent's[2] absolute measurements at lower pressures for ethylene saturated with mercury at $0°$ to give a hydrogen quantum yield of 3.9×10^{-3} at 70 cm. The quantum yields for other products found in the current work at this ethylene pressure may then be calculated. The quantum yields for cyclobutane, butene-1, butane, butadiene, hexene-1, and hexane are then found to be 3.8×10^{-6}, 48×10^{-6}, 1.34×10^{-4}, 46×10^{-6}, 2.3×10^{-4}, and 1.3×10^{-4}, respectively. Absolute values are probably not valid to better than ± 50 or 100%. At a typical total light input of 0.14 einstein/mole of ethylene, the limits of detection set for $C_2H_2D_2$ correspond to a quantum yield for this species of less than 7×10^{-4}, or *less* than 100 molecules of $C_2H_2D_2$ formed per molecule of cyclobutane $C_4H_4D_4$ found as a product at a total ethylene pressure of 74 cm. The 112 kcal./einstein mercury excitation gives 131 kcal./mole as a maximum possible value for the excess energy of a cyclobutane molecule, 68 kcal. above the barrier to decomposition to ethylene, assuming no partial deactivation of excited ethylene or tetramethylene intermediates. Thus, if the addition of triplet ethylene to ground state ethylene is an efficient process, followed by an efficient triplet–singlet transition of the tetramethylene to a highly vibrationally excited cyclobutane, this cyclobutane would be expected to have a very short and pressure-dependent lifetime before reversion to ethylene. The upper bound of 7×10^{-4}

(6) We are indebted to Dr. Colin MacKay for this analysis.

(7) A. B. Callear and R. J. Cvetanović, *J. Chem. Phys.*, **24**, 873 (1956).