Effect of Stirring on the Distribution Equilibria of *n*-Alkyl-Substituted Dithizones

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Abstract: Reversible changes in the distribution ratios of *n*-alkyl-substituted dithizones were caused by high-speed stirring. The extent of the change was affected by the pH of the aqueous phase, by the size of the alkyl group, and by the organic solvent. Interfacial tension measurements suggested the preferential adsorption of the anion form on the interface. The distribution process during stirring can be rationalized in terms of interfacial adsorption of the solutes.

Introduction

Shaking or agitation of a two-phase liquid-liquid system is, of course, employed to speed the equilibration of the reaction mixture. The concept of equilibrium requires that once the phases have been equilibrated the distribution ratio of any distributing solute remain constant regardless of the degree of agitation. We were therefore quite surprised to observe a reversible color change in di(*p*-butylphenyl)thiocarbazone (butyldithizone) in *n*-hexane/alkaline (pH 10.5) aqueous solution system that occurred when the mixture was shaken. During shaking, the green color characteristic of the neutral compound changed to a mixture of orange and green, indicating the presence of the anion form as well. When the shaking stopped, the mixture reverted in a second to the original green organic and colorless aqueous phase.[1] The distribution ratio, *D*, of a chelating ligand, HL, which is a weak acid, is represented by

$$D = \frac{K_D H}{H + K_a} \tag{1}$$

where K_D and K_a refer to the distribution and acid dissociation constants, respectively, and H refers to the hydrogen ion concentration. The values of the ratio of K_D/K are determined from the measurements of D as a function of pH values in the range pH $\gg$ pK.

In this study, we intend to examine the cause of the reversible color change caused by shaking. The new distribution apparatus built recently by us allows us to measure absorbance changes in the organic phase during high-speed stirring.[2]

Experimental Section

Chemicals. Diphenylthiocarbazone (Dz) was used after purification.[3] Di(*p*-tolyl)thiocarbazone (MeDz) (methyldithizone) was synthesized previously in our laboratory. *p*-Ethyldithizone (EtDz) and *p*-butyldithizone (BuDz) were synthesized by the method of Hubbard and Scott.[4] Elemental analysis for C, H, and N and spectral data were used to identify these compounds. *p*-Hexyldithizone (HexDz) was kindly supplied by Dr. Uesugi of Himeji Institute of Technology, Japan. The organic solvents used, which include *n*-hexane, carbon tetrachloride, benzene, and chloroform, were all analytical reagent grade. Chloroform was washed three times with water just before use. Phosphate buffer and sodium hydroxide solutions, both prepared from AR reagents, were washed with BuDz-chloroform solution to remove any metal ion impurities. Deionized water was used throughout the experiment.

Distribution Experiments. The apparatus used has been described elsewhere in detail.[2] In the present work, a 10-mm path length flow cell (0.29 mL) was used in the place of 50-μL glass capillary cell used for the kinetic experiment. The volume of liquid thus removed at any one time from the distribution vessel is 1.4 mL.

Fifty milliliters of organic phase, including the reagent in the order of 10^{-5} M concentration, is introduced into the distribution vessel and the pump is started. The organic phase passes through the flow cell attached to the Gilford Model 2400 spectrophotometer and returns to the vessel. After the absorbance reading on the recorder reaches a steady value, 50 mL of the aqueous phase, buffered with phosphate-NaOH solution and adjusted to an ionic strength of 0.1 with $NaClO_4$, is added into the flask. Stirring is started and the absorbance change is continuously recorded at λ_{max} of the reagent. All measurements have been carried out at 25 ± 0.1 °C.

Interfacial Tension Measurements. Interfacial tension, γ_i, between the aqueous and organic phases, which include carbon tetrachloride or chloroform solutions of Dz or BuDz, was measured by means of the drop-volume method at 25 ± 0.1 °C.[5] The apparatus consists of a 200-μL Gilmont micrometer buret and a glass capillary tip vertically placed in the center of a 40-mL vial which contains 20 mL of the aqueous phase. Reproducibility in γ_i measurement was within 2%.

Results and Discussion

A typical example of the distribution change with stirring is shown in Figure 1. The absorbance decreases within 1 or 2 s after the start of stirring and recovers equally rapidly when stirring stops. The extent of decrease in absorbance clearly increased with increase of pH.

Stirring speed also was one of the factors governing the extent of change. As shown in Figure 2, the absorbance decreased with increase of stirring speed which is indicated by the voltage supplied to the stirrer motor. However, above 45 V it became constant. This probably means that the system achieved the maximum degree of dispersion as determined by the solvent system and the configuration of the apparatus. Hence, a value of 50 V was adopted throughout the remainder of the study.

From the initial absorbance of organic phase (A_o) and the absorbance decrease (ΔA) caused by stirring, the apparent distribution ratio, D', under the high-speed stirring, can be calculated as

$$D' = \frac{A_o - \Delta A}{\Delta A} \tag{2}$$

The apparent distribution ratios were measured as a function of pH for each alkyldithizone using chloroform as the organic solvent. As shown in Figure 3, log D' values decrease with increasing pH with unit slope for every reagent system. Apparent distribution ratios were also measured for the other solvent systems of *n*-hexane, carbon tetrachloride, and benzene.

The value of D' appeared to be independent of the concentration of alkyldithizone in the concentration range studied. No significant change was observed in the ranges of 6×10^{-6} to 5×10^{-5} mol/L of butyldithizone in hexane/water at pH 8.44 and 0.1 ionic strength.

From the distribution data, $pH_{1/2}$ values for the reagents were calculated and summarized in Table I along with the values obtained with no stirring.

Interfacial tension (γ_i) measurements were carried out with aqueous phases at two pH values, pH 3.5 and 12.0, and the

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(1) Although it has been pointed out (K. A. Allen and W. J. McDowell, *J. Phys. Chem.*, **64**, 877 (1960)) that, in systems involving high surfactant concentrations, even relatively mild stirring (100 strokes/min) can give rise to spurious, long-lasting metastable states, this phenomenon is distinctly different.

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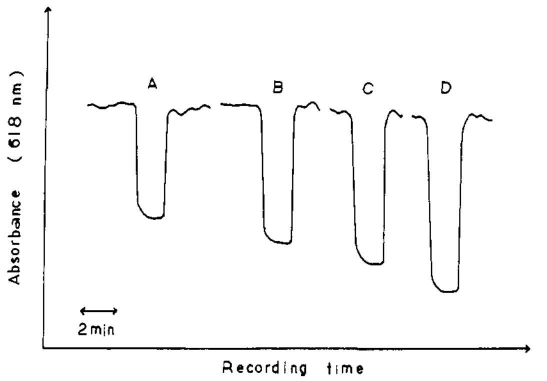


Figure 1. Reversible absorbance change in organic phase caused by stirring in the system of BuDz in $CHCl_3/H_2O$ (I = 0.1): (A) pH 11.56; (B) pH 11.73; (C) pH 11.87; (D) pH 11.93.

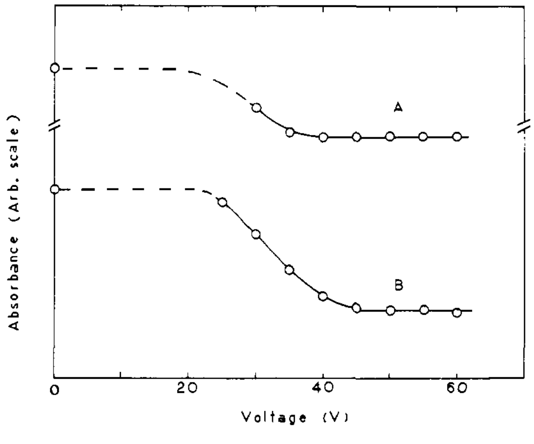


Figure 2. Change in absorbance as a function of stirring speed in terms of the voltage supplied to stirring motor: (A) HexDz in $CHCl_3$/pH 12.0; (B) BuDz in *n*-Hex/pH 10.5.

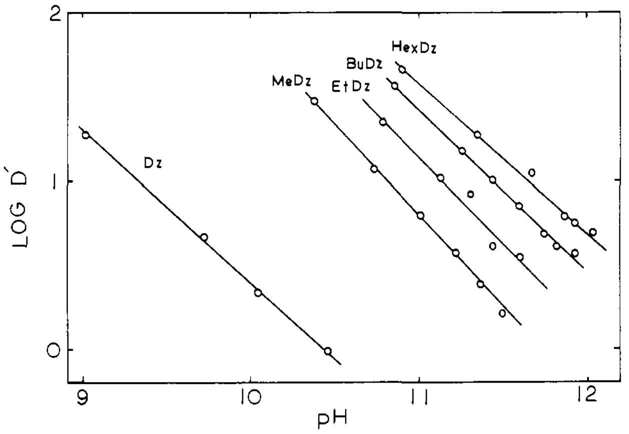


Figure 3. Apparent distribution ratio under high-speed stirring.

following organic phases: Dz in $CHCl_3$, BuDz in CCl_4, and BuDz in $CHCl_3$. In the acidic systems there was no change in γ_i value that could be attributed to the presence of the solute. In the alkaline systems, however, a decrease in γ_i was observed with increase of solute concentration as shown in Figure 4. The maximum slopes of these curves were used to estimate the surface area occupied by one solute molecule, A, according to the Gibbs adsorption isotherm

$$A = -kT/\left(\frac{\partial \gamma_i}{\partial \ln c}\right)_T \qquad (3)$$

where k is the Boltzmann constant and C is the concentration of solute. The estimated values for A (Å^2/molecule) were 90 for Dz in $CHCl_3$, 70 for BuDz in CCl_4, and 150 for BuDz in $CHCl_3$.

Table I. Summary of the Effect of Stirring on the Distribution of *n*-Alkyl-Substituted Dithizone at 25 °C

reagent	solvent	$pH_{1/2}$ no stirring	$pH_{1/2}$ high-speed stirring	$\Delta pH_{1/2}$
Dz	$CHCl_3$	10.43 (0.93)[a]	no change	0
MeDz	$CHCl_3$	11.90 (1.06)	11.74 (1.11)	0.16
EtDz	$CHCl_3$	12.80 (0.86)	12.13 (1.00)	0.67
BuDz	$CHCl_3$	15.50[b]	12.50 (0.95)	3.00
HexDz	$CHCl_3$	17.80[c]	12.78 (0.89)	5.02
BuDz	*n*-Hexane	12.80[b]	8.89 (0.66)	3.91
BuDz	CCl_4	13.75[b]	12.90 (0.50)	0.85
BuDz	benzene	13.85[b]	12.71 (0.85)	1.14

[a] Slope of log D vs. pH plot is in parentheses. [b] Reference 8. [c] Reference 9.

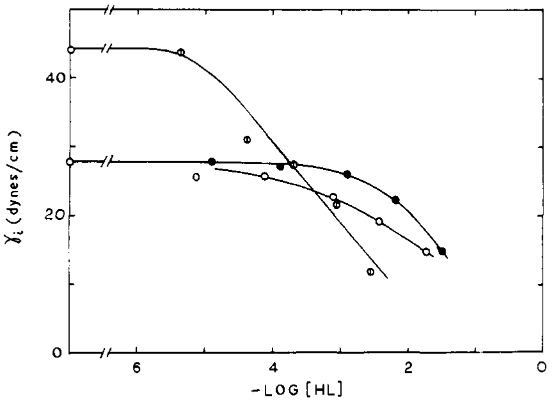
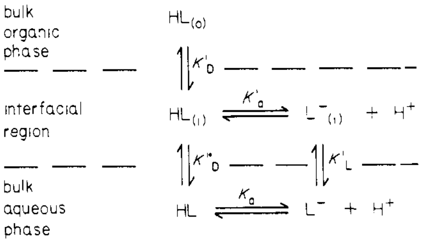


Figure 4. Interfacial tension vs. log concentration curves: (◐) BuDz in CCl_4 (pH 11.95); (●) Dz in $CHCl_3$ (pH 11.96); (○) BuDz in $CHCl_3$ (pH 11.75).

The minimum solute concentration required for interfacial saturation, C_m, can also be obtained from Figure 4. The estimated values for log C_m were −2.2 for Dz in $CHCl_3$, −3.7 for BuDz in CCl_4, and −2.8 for BuDz in $CHCl_3$. As might be expected, the greater effect is observed in the poorer solvent. The decrease in interfacial tension under alkaline but not acid conditions suggests that it is the reagent anion rather than the nonionized reagent that is surface active.

The reversible concentration change in the organic phase, which was caused by stirring, suggests a significant participation of the liquid–liquid interface in the equilibrium. On the basis of these observations, the following distribution mechanism is suggested



(4)

where

$$K_D = [HL]_o/[HL] \qquad (5)$$

$$K_a = [H^+][L^-]/[HL] \qquad (6)$$

$$K_D' = [HL]_o/[HL]_i \qquad (7)$$

$$K_D'' = [HL]_i/[HL] \qquad (8)$$

$$K_L' = [L^-]_i/[L^-] \qquad (9)$$

$$K_a' = [H^+][L^-]_i/[HL]_i \qquad (10)$$

and subscripts o and i refer to organic and interfacial phases.

A further relation can be derived

$$K_aK_D'' = K_a'K_L' \qquad (11)$$

In this formulation, the interfacial region is pictured as a polar liquid more nearly like water than organic solvent with H^+ freely and equivalently moving between the interfacial and aqueous phases.

Since the concentration of solute (10^{-5} M) employed is much lower than C_m as well as being in the concentration range where D' is independent of concentration, ideal adsorption isotherms were postulated for the reactions (eq 7–9) involving the interface. Also, even under high-speed stirring, the volumes of organic and aqueous phases, V_o and V_a, much larger than the volume of interfacial phase, Ad, where A and d refer to the interfacial area and the thickness of the interfacial region, are assumed not to change appreciably under high-speed stirring.

Equations 5–12 and the following mass balance equation

$$[HL]_{o,init}V_o = [HL]_o'V_o + \{[HL]_i + [L^-]_i\}Ad + \{[HL] + [L^-]\}V \qquad (12)$$

give the following expression for the apparent distribution ratio as defined in eq 2.

$$D' = \frac{[HL]_o}{[HL]_{o,init} - [HL]_o} \qquad (13)$$

$$D' = \frac{K_D\left\{\dfrac{H}{H + K_a}\right\}\dfrac{V_o}{V}}{K_D''\left\{\dfrac{H + K_a'}{H + K_a}\right\}\dfrac{Ad}{V} + 1} \qquad (14)$$

From the expression (eq 1) for the distribution ratio obtained in the absence of stirring, D, we obtain, provided the bulk phase volume ratio is unity

$$\frac{D}{D'} = K_D''\left\{\frac{H + K_a'}{H + K_a}\right\}\frac{Ad}{V} + 1 \qquad (15)$$

which, at pH values much higher than pK_a' or pK_a, simplifies, with the help of eq 12, to

$$\frac{D}{D'} = K_L'\frac{Ad}{V} + 1 \qquad (16)$$

The change observed in $pH_{1/2}$ values with stirring is log D/D', so that

$$\log\frac{D}{D'} - 1 = \log(10^{\Delta pH_{1/2}} - 1) = \log K_L' + \log\frac{Ad}{V} \qquad (17)$$

From eq 17, the drop in $pH_{1/2}$ with stirring is seen to depend on the distribution of the anion between the interfacial and bulk aqueous phases as well as the relative amount of interface generated by stirring, Ad/V. With the same experimental configuration, Ad/V reaches essentially the same maximum value, permitting the observed $pH_{1/2}$ values to be related to the structural changes in the alkyldithizone. (See Figure 5.)

The value of the distribution constant of the anion between the interfacial and aqueous phases, K_L', can be expected to change in a regular manner with increasing number of methylene groups in a homologous series of dithizonates.[6] Thus

$$\log K_L' = \log K'_{L(DZ^-)} + 2n\pi_{CH_2} \qquad (18)$$

where $K'_{L(DZ^-)}$ refers to the distribution constant of the parent dithizone anion, π_{CH_2} the incremental increase in distribution constant per methylene group, and $2n$ is the number of such groups, e.g., 2 for methyl and 4 for ethyl (since the dithizone is symmetrically disubstituted). Hence eq 17 may be rewritten as

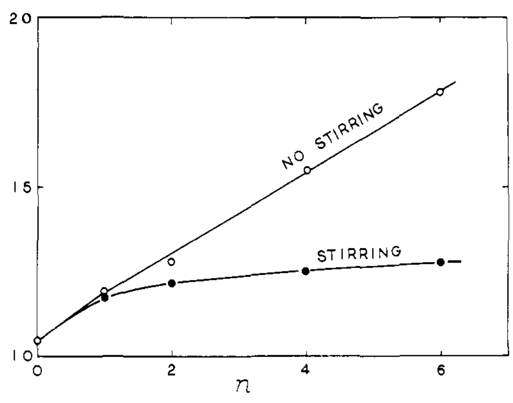


Figure 5. Variation of $pH_{1/2}$ with the number of carbon atoms.

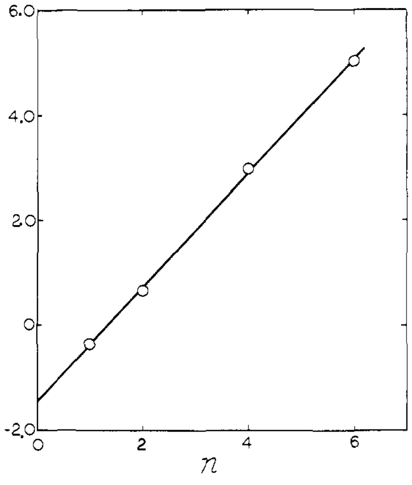


Figure 6. Plot of $\log(10^{\Delta pH_{1/2}} - 1)$ vs. length of alkyl group, n.

$$\log(10^{\Delta pH_{1/2}} - 1) = 2n\pi_{CH_2} + \log K'_{L(DZ)}\frac{Ad}{V} \qquad (19)$$

A plot of $\log(10^{\Delta pH_{1/2}} - 1)$ vs. n is linear (Figure 6) with a slope and intercept of

$$\pi_{CH_2} = 0.56 \qquad (20)$$

$$\log K'_{L(DZ)}\frac{Ad}{V} = -1.57 \qquad (21)$$

The value of 0.56, corresponding to 0.76 kcal/mol, is in good agreement with the value of 0.81 kcal/mol reported for the transfer of a methylene group from the interface to the aqueous phase.[7] Equation 21 signifies that even for dithizonate, the contribution of the interfacial effect is present, although very small (2.6%). The interfacial component as calculated from eq 20 and 21 rises rather rapidly from 26% in MeDz to 82% in EtDz, 99.9% in BuDz, and to all but 7×10^{-4}% in hexyldithizone.

Uncovering the contribution of interfacial participation in extraction equilibria involving higher molecular weight analogues of dithizone will be useful in understanding distribution phenomena of a wide variety of hydrophobic species. Similar studies can be of invaluable assistance in quantitative assessment of the role of the interface in liquid–liquid systems. For example, the distribution of an alkyldithizone, e.g., butyldithizone, can be used as

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a probe of the influence of other substances in replacing it in the interfacial region. Further, elucidation of the kinetics and mechanism of extraction of metal chelates of higher molecular weight extractants absolutely requires the fundamental information obtained by such studies. Work addressing these opportunities is now underway in our laboratory.

Acknowledgment. The project was supported by a grant from the National Science Foundation.

Registry No. Dz, 60-10-6; MeDz, 16026-13-4; EtDz, 83454-27-7; BuDz, 65388-10-5; HexDz, 70857-97-5; $CHCl_3$, 67-66-3; CCl_4, 56-23-5; benzene, 71-43-2; *n*-hexane, 110-54-3.

The Dimers of Carbon Monoxide and Carbon Monosulfide. Chemically Bound Triplet Electronic Ground States

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Abstract: The $^3\Sigma_g^-$ electronic ground states of OCCO and SCCS have been studied by using nonempirical molecular electronic structure theory. Reasonably large double-ζ plus polarization (DZ + P) basis sets have been used throughout and are designated C,O(9s5p1d/4s2p1d), S(11s7p1d/6s4p1d). Geometrical structures and vibrational frequencies were determined at the self-consistent-field level of theory and relative energies from explicitly correlated wave functions. The structures of $^3\Sigma_g^-$ ethylenedione and ethylenedithione lead one to anticipate strong chemical bonds. The predicted vibrational frequencies also support this general view. For both C_2O_2 and C_2S_2, the $^3\Sigma_g^-$ electronic states are minima on their respective potential energy hypersurfaces. In each case the $^3\Sigma_g^-$ state lies below the lowest spin-allowed dissociation limit, $X^1\Sigma^+ + a^3\Pi$: for C_2O_2 the predicted dissociation energy is 74 kcal and for C_2S_2, 119 kcal. Furthermore, triplet ethylenedithione is predicted to be the absolute minimum on the C_2S_2 energy surface, lying 39 kcal below $X^1\Sigma^+$ CS + $X^1\Sigma^+$ CS.

Introduction and Qualitative Analysis

It has long been appreciated[1] that it is possible to write down a plausible valence structure for the carbon monoxide dimer $(CO)_2$. The chemical name ethylenedione is readily seen to be applicable to structure **1**. The existence of valence structure **1** suggests a

$$O{=}C{=}C{=}O$$

1

close-shell singlet electronic ground state, and this arises from the electronic configuration

$$^1\Sigma_g^+ \qquad 1\sigma_g^2 1\sigma_u^2 2\sigma_g^2 2\sigma_u^2 3\sigma_g^2 3\sigma_u^2 4\sigma_g^2 4\sigma_u^2 5\sigma_g^2 1\pi_u^4 1\pi_g^4 5\sigma_u^2$$

2

Nevertheless, all efforts, beginning as early as 1913, to prepare a chemically bound C_2O_2 species have proven unsuccessful.[2-7] $(CO)_2$ does of course exist as a van der Waals molecule, but its dissociation energy appears to be less than 1 kcal/mol.[8] The cation $(CO)_2^+$ is reasonably well characterized experimentally and has a dissociation energy D_0 (OC–CO$^+$) = 22 ± 1 kcal,[9] indicative of considerably less than a true carbon–carbon single bond.

Theoretical studies have shown[1,10-14] that the ground-state electron configuration of C_2O_2 is not **2** but rather

$$^3\Sigma_g^- \; ^1\Delta_g, ^1\Sigma_g^+ \qquad 1\sigma_g^2 1\sigma_u^2 2\sigma_g^2 2\sigma_u^2 3\sigma_g^2 3\sigma_u^2 4\sigma_g^2 4\sigma_u^2 5\sigma_g^2 1\pi_u^4 1\pi_g^4 2\pi_u^2$$

3

Hund's rules then require the lowest electronic state of the open-shell configuation **3** to be the $^3\Sigma_g^-$ state. Moreover, a triplet ground state of C_2O_2 might be more difficult to detect experimentally than an ordinary closed-shell singlet (note of course that ESR experiments would be more suitable for a triplet ground state). However, a point that does not appear to have be given proper emphasis is the fact that $^3\Sigma_g^-$ C_2O_2 is a genuine chemically bound system. In the absence of spin–orbit coupling (which should be small for a molecule as light as ethylenedione), the ground triplet state is forbidden by spin conservation to dissociate to two ground-state carbon monoxide molecules:

$$^3\Sigma_g^- \; C_2O_2 \rightarrow {}^1\Sigma^+ \; CO + {}^1\Sigma^+ \; CO \qquad (1)$$

The lowest energy dissociation limit available for C–C bond rupture involves the lowest triplet state of CO, and inspection of (2) shows that this dissociative channel is symmetrically allowed

$$^3\Sigma_g^- \; C_2O_2 \rightarrow {}^1\Sigma^+ \; CO + {}^3\Pi \; CO \qquad (2)$$

only for nonlinear pathways. Since the $a^3\Pi$ state of CO lies 48 687 cm^{-1} = 139 kcal[15] above the $X^1\Sigma^+$ ground state, it is implicit in earlier theoretical studies that the $^3\Sigma_g^-$ ground state of C_2O_2 could be quite stable with respect to C–C dissociation. One can, however, envision a predissociative mechanism that might yield a relatively short lifetime for $^3\Sigma_g^-$ C_2O_2. The spin–orbit coupling might be large enough if a potential curve crossing occurs not too far from the minimum in the $^3\Sigma_g^-$ state (e.g., by a $^1\Sigma^+$ state

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